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X-Ray Study of Benzene-Cyclohexane Mixtures

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X-ray diffraction patterns have been made of benzene, cyclohexane, and three mixtures. The first strong peak of the mixtures is a single peak showing no trace of resolution into a benzene peak and a cyclohexane peak. If benzene-cyclohexane mixtures have an emulsion type of structure, such as postulated by H. K. Ward, the separation of the benzene and cyclohexane peaks is too small, relative to the peak widths, to allow the two component peaks to be distinguished. X-ray studies of benzene-cyclohexane mixtures can neither prove nor disprove the existence of an emulsion type of structure in the mixture.

INTRODUCTION

BENZENE and cyclohexane each have a very strong first peak in their x-ray scattering curves. In a study of mixtures of benzene and cyclohexane, H. K. Ward[1] has reported that the scattering curve of the mixture shows the individual peaks of the two components. From this it has been concluded that solutions of benzene and cyclohexane have an emulsion type of structure. The liquid is pictured as consisting of small clusters of either benzene or cyclohexane molecules. The diffraction pattern of the mixture would then be a superposition of the patterns of the two components.

Since these two liquids are considered to be highly soluble in one another, this result is unexpected, and one is justified in asking that the experimental results, upon which the conclusion is based, be very definite. A number of points in Ward's work are open to criticism. The benzene peak is drawn in as though it came up to a sharp point. Actually liquid peaks are rounded at the top similar to an error curve. The two component peaks are so close together, that the experimental points must be known with extreme accuracy to justify drawing in two peaks rather than a single smooth peak. Actually a number of the experimental points deviate from the curve which has been drawn by more than the amount which distinguishes a single peak from the double peak.

EXPERIMENTAL

X-ray diffraction patterns were made in a cylindrical camera of radius 8.67 cm. The radiation was Cu $K\alpha$ $\Lambda = 1.539$A, filtered with nickel foil. The primary beam was collimated by two pin holes 0.50 mm diameter, separated 8.0 cm. The liquids were contained in a flat cell faced with Cellophane windows, and 1.6 mm thick. The benzene was stockroom pure material. Two samples of cyclohexane were used; Eastman pure and a sample specially purified.* No differ-

[1] H. K. Ward, J. Chem. Phys. **2**, 153 (1934).

* We are indebted to Professor G. Scatchard for the specially purified cyclohexane.

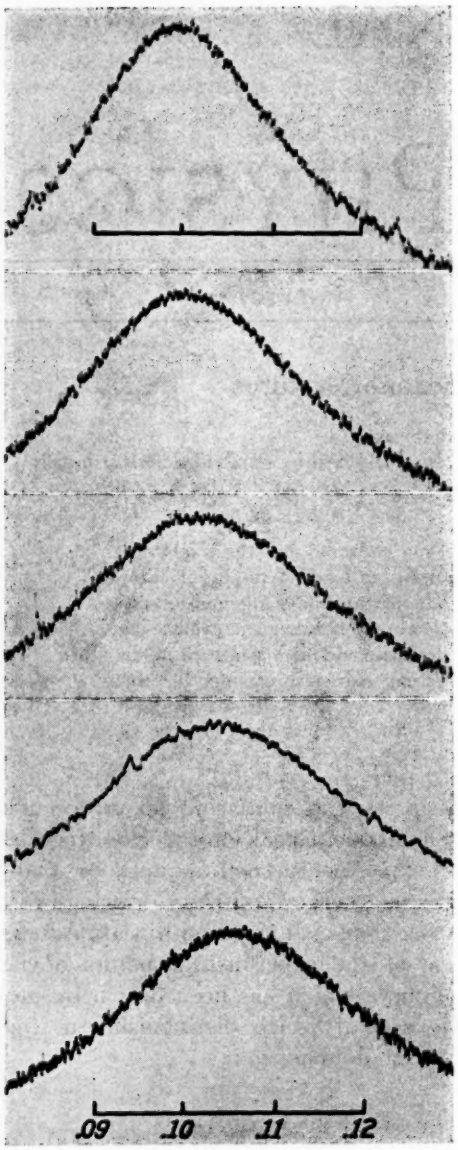

FIG. 1. Microphotometer records of the first strong peak for benzene, cyclohexane and three mixtures. Values of sin θ/Λ are given as abscissae.

ence could be detected in the patterns of the two cyclohexane samples.

Diffraction patterns were made of benzene, cyclohexane, and three mixtures. The compositions of the five samples are given in Table I. Exposures were of the order of four hours. The films were microphotometered using an enlarging ratio of 6.8. From Ward's results for benzene and cyclohexane, it can be calculated that for a camera of radius 8.67 cm, the separation between the benzene and cyclohexane peaks should be 2.2 mm on the film, or 14.9 mm on the microphotometer record.

RESULTS

Figure 1 shows the microphotometer records of the first strong peak in the diffraction patterns of the five samples studied. The benzene peak occurs at sin $\theta/\Lambda=0.1057$, and the cyclohexane peak at 0.0996. For the three benzene-cyclohexane solutions, there is no sign of resolution into a benzene and a cyclohexane peak. For each composition there appears only a single peak whose position shifts with the composition. The value of sin θ/Λ for the peak is given in Fig. 2 in terms of a length d defined by the relation $d=1/(2 \sin \theta/\Lambda)$. The length d is proportional to intermolecular separations, and as seen from Fig. 2, does not vary linearly with composition.

DISCUSSION

According to Ward's emulsion picture of a benzene-cyclohexane mixture, the main peak of the mixture should be given by compounding the patterns of benzene and cyclohexane weighted with respect to the composition. A separation of the peak for a mixture into two component peaks is not shown by the microphotometer records of Fig. 1. While this result furnishes no evidence for the existence of the emulsion type of solution, it should be emphasized that it does not necessarily disprove it. Assuming an emulsion type of solution, the peak for a mixture should be given by compounding the peaks of the two components. However, it is not evident whether the compounded peak will show the two peaks out of which it is compounded, or whether the two component peaks will merge into a single peak. Which will be the case,

TABLE I. *Composition of samples in percent cyclohexane.*

LIQUID	PERCENT VOLUME	PERCENT WEIGHT
Benzene	0.0	0.0
Solution No. 1	25.0	22.8
Solution No. 2	50.0	47.0
Solution No. 3	75.0	72.8
Cyclohexane	100.0	100.0

depends upon the sharpness of the component peaks relative to their separation.

A rough answer to the question can be obtained by approximating the peaks by error curves. Two similar error curves having a half-maximum width W and a separation S, if compounded will show resolution into two component peaks only if $S/W>0.9$. Expressed in terms of $\sin\theta/\Lambda$, Ward's results give $S=0.1064-0.0983=0.0081$ and an average $W=0.0278$. For benzene-cyclohexane mixtures the ratio is $S/W=0.29$. Since this is only about one-third of the value necessary for the beginning of resolution, we would not expect the compounded peak to show the existence of the two component peaks.

The fact that the peak for a 50-50 mixture cannot show the two component peaks is illustrated by Fig. 3. The curves C and B are the cyclohexane and benzene experimental intensity curves obtained directly from the microphotometer records. The upper curve is one-half the sum of curves B and C, obtained by direct addition of the ordinates at the indicated points. There is no indication of two component peaks in the compounded curve.

X-ray diffraction patterns of benzene-cyclohexane mixtures show only a single strong peak. There is no trace of individual benzene and cyclohexane peaks. The position of the single peak shifts continuously with the composition. The ratio of peak separation to peak width is so small that x-ray studies of benzene-cyclohexane mixtures can neither prove nor disprove the existence of an emulsion type structure.[2]

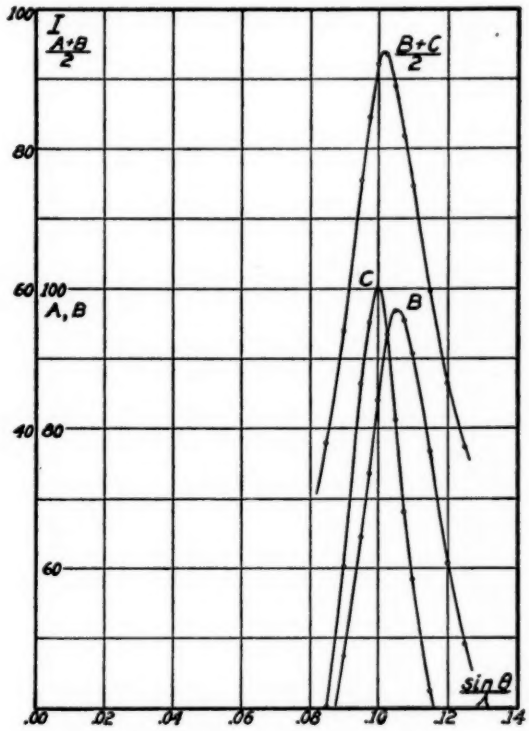

FIG. 3. Lower curves B and C: experimental intensity curves for benzene and cyclohexane. Upper curve: one-half the sum of curves B and C.

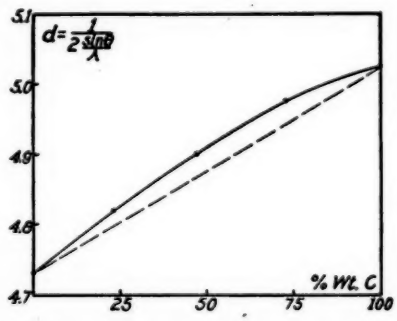

FIG. 2. Position of first peak for benzene-cyclohexane mixtures as a function of composition. The value of $\sin\theta/\Lambda$ for the peak is expressed in terms of a length d.

[2] Vapor pressure measurements show that an emulsion type structure is extremely improbable. "Vapor-Liquid Equilibrium III. Benzene-Cyclohexane Mixtures," G. Scatchard, S. E. Wood, and J. M. Mochel, J. Phys. Chem. **43**, 119 (1939).

The Diffraction of X-Rays by Gas Molecules

A Comparison with Electron Diffraction and a Discussion of the Results for $SiHCl_3$

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The principles of x-ray and electron diffraction by free molecules are discussed in view of the application of these methods to the determination of molecular structures. The influence of the chemical bond is not more disturbing for x-ray measurements than for electron measurements. The hydrogen atoms are practically nonexistent for x-ray diffraction while it is not so for electron diffraction. This is an advantage which has not yet been fully used. The following procedure is suggested: first an x-ray investigation in which the number of parameters to be determined is much reduced, and subsequently an electron investigation which will determine the remaining parameters, i.e., the position of the hydrogen atoms. Thus in some cases at least (CH_3Cl e.g.), the use of both diffraction methods is necessary and is sufficient for determining completely the molecular structure, including the position of the hydrogen atoms. A discussion of x-ray measurements on $SiHCl_3$ shows the precision and the certainty of the method. As for the disadvantages of the long times of exposure, which have been more than 100 hours, they have been reduced to, say, 8 hours for crystal-monochromatized radiation and they will probably be reduced by a new factor 10 in the near future. Although being less numerous than in the case of electron diffraction, the maxima given by x-ray diffraction present two fundamental advantages. In general they are actual, well-defined maxima. The effect of molecular vibrations on them, which is difficult to calculate, is the smallest just at the angles at which they are the most prominent.

ALTHOUGH important investigations have been made, especially by the school of Debye, on the diffraction of x-rays by polyatomic gases, this method is very far from being so extensively used as the electron diffraction method for determining molecular structures. The electron method is often considered as more convenient. But there remain also misunderstandings as to the fundamental possibilities of the x-ray method, especially as to its precision. Therefore, we consider it desirable to discuss this matter again, and to show that we can take advantage of the fact that it is impossible to locate the H nuclei by x-ray diffraction, while it is not so by electron diffraction.

Scattering by Atoms

If an atom is submitted to the alternating electromagnetic field of an x-ray wave whose amplitude is A_0, its electrons scatter a secondary wave (coherent radiation) whose amplitude A is given by

$$A = A_0\left(\frac{1}{R}a_e f\right)\sin\alpha. \qquad (1)$$

α is the angle between the direction of the electric vector of the primary wave and the direction of the scattered wave; R is the distance between the atom and the point of observation; a_e is the classical radius of the electron, $a_e=\epsilon^2/\mu c^2 = 2.8\times10^{-13}$ cm; ϵ and μ being respectively the charge and the mass of the electron and c the velocity of light; f is called the atomic scattering factor; it is, by definition, the ratio of the amplitude scattered by the atom to the amplitude a "free electron" should scatter, in the same conditions, according to the classical theory of J. J. Thomson. In general, f is a function of the variable $(\sin\theta/2)/\lambda$ only; the scattering angle θ being the angle between the primary and the secondary ray, and λ being the wave-length. At very small angles θ, f is equal to the atomic number Z of the atom.[1]

The intensity of an electron ray, which is proportional to the number of electrons passing through unit surface in unit time, is given by the square of its "amplitude," according to wave mechanics. If a homogeneous beam of rapid electrons of amplitude A_0 hits an atom, the scattered amplitude A is given by:[2]

$$A = -A_0\frac{1}{R}\frac{\epsilon^2}{E}\frac{1}{s^2}(Z-f), \qquad (2)$$

* C.R.B. Belgian Graduate Fellow, Princeton 1938–1939; formerly at the University of Liège, Belgium.

[1] P. Debye, Physik. Zeits. **31**, 419 (1930).
[2] N. F. Mott, Proc. Roy. Soc. **A127**, 658 (1930).

where $s=2\sin\theta/2$, E is the energy of each incident electron, f is the atomic scattering factor which has been already defined for x-rays, λ is the de Broglie wave-length which, neglecting the relativity correction, is given, in angstroms, by the formula

$$\lambda=\left(\frac{149.55}{V}\right)^{\frac{1}{2}}, \tag{3}$$

where V is the accelerating potential of the electrons in volts.

As the electron radius a_e is very small, the scattered x-ray amplitude is also small in comparison with the primary amplitude. But for the fact that f varies with the wave-length λ, while, however, retaining in general the same order of magnitude, the scattered x-ray amplitude should be independent of λ. On the contrary, the scattered electron amplitude not only depends on f, but depends also explicitly on the energy E of the incident electrons, i.e., on the de Broglie wave-length λ. If we take the case where $\sin\alpha$ and s are equal to unity, the importance of the interaction of x-rays and electrons with matter is then chiefly determined by the values of a_e and ϵ^2/E; the interaction will be nearly the same for both kinds of diffraction when the energy of the electrons is such that

$$a_e=\epsilon^2/E=\epsilon/V,$$

i.e., for an accelerating potential of the electrons equal to $V=\epsilon/a_e=(4.8\times10^{-10}\times300)/(3\times10^{-13})$ i.e., half a million volts. For such a potential the wave-length is about 0.017A. The usual potentials are about 50,000 volts, which corresponds to $\lambda=0.055$A; for such energies $\epsilon^2/E=(4.8\times10^{-10}\times300)/(5\times10^4)\approx3\times10^{-12}=10a_e$, the amplitude is 10 times greater for electrons than for x-rays. But for electrons of 1.5 million volts and 0.01A wave-length, the factor ϵ^2/E is only $a_e/3$; the scattered amplitude should be three times smaller for electrons than for x-rays in this case. These data are only valid for $s=1$, which corresponds to a scattering angle $\theta=60°$; it must be borne in mind that, on account of the term s^{-2} in formula (2), the electron amplitude is much greater at smaller angles θ: at $\theta=10°$ the scattered amplitude is 30 times more than at 60°. In short, the intensity of interaction with matter is under the usual conditions greater for electrons than for x-rays, but it is no more so for great scattering angles and very rapid electrons.* Slow electrons, on the other hand, are not suitable for structure determination; the theory of scattering assumes that the kinetic energy of the incident electrons is greater than the bonding energy of the K electrons of the atom, and this sets an upper limit of, say, 0.1A to the electron wave-lengths which can be used. The x-ray wave-lengths which are generally used measure about 1A; for example Cu $K\alpha$: 1.54A and Mo $K\alpha$: 0.71A; as the dimensions of the atoms and molecules are of this order of magnitude, they are sufficient for giving good interference effects. Shorter wave-lengths could, however, be used.

Atomic scattering factors

The atomic scattering factors f for x-rays are calculated on the main assumption of Schrödinger's continuous electronic atmosphere in the atom, each volume element of this atmosphere being considered as scattering light according to the classical theory. The complete wave-mechanical treatment of the problem of the coherent and incoherent scattering justifies this treatment.[3] The numerical calculations are founded on approximations made on the electronic distribution in the atom, as this cannot be exactly calculated for other atoms than the H atom. All these approximations consider the electronic atmosphere as spherically symmetric; it is generally admitted that the best one is given by Hartree's method of the self-consistent field.[1] The calculated values agree well with the most careful measurements.[4]

In the case of electron diffraction, we can also define an atomic scattering factor F;[2] the formula (2) can be written in the following way

$$A=-A_0\frac{2}{a_H}\frac{1}{R}\frac{Z-f}{k^2s^2}, \tag{4}$$

* In a given range of $(\sin\theta/2)/\lambda$ values, x-ray and electron diffraction by gas molecules give the same number of intensity "maxima." As the electron wave-lengths are usually much shorter than the x-ray wave-lengths, a given number of "maxima" will be found in a much smaller range of θ angles for the electron diffraction.

[3] G. Wentzel, Zeits. f. Physik **43**, 779 (1927); I. Waller, Phil. Mag. **4**, 1228 (1927).

[4] E. O. Wollan, Rev. Mod. Phys. **4**, 205 (1932); G. Herzog, Helv. Phys. Acta **6**, 508 (1933).

where $k=2\pi/\lambda$ and a_H is the Bohr radius of the H atom, which is given by the formula

$$a_H=\frac{h^2}{4\pi^2\mu\epsilon^2}=0.53\times10^{-8}\text{ cm},$$

where h is Planck's constant.

The expression

$$F=(Z-f)/k^2s^2 \qquad (5)$$

is called the atomic scattering factor for electrons. F plays in formula (4) a rôle analogous to the rôle f plays in formula (1) and it is readily calculated from the values of f. Fig. 1, which represents for the argon atom the values of f and F plotted against $(\sin\theta/2)/\lambda$, shows the difference of behavior of these two functions: both decrease with increasing $(\sin\theta/2)/\lambda$, but the decrease is more rapid for F than for f, at least in the beginning of the curve.

It is interesting to compare the x-ray scattering factor per electron f/Z of a given atom with the function $(Z-f)/Z=1-f/Z$. This function is equal to the ratio of the scattering factor of the atom for electron rays, to the scattering factor

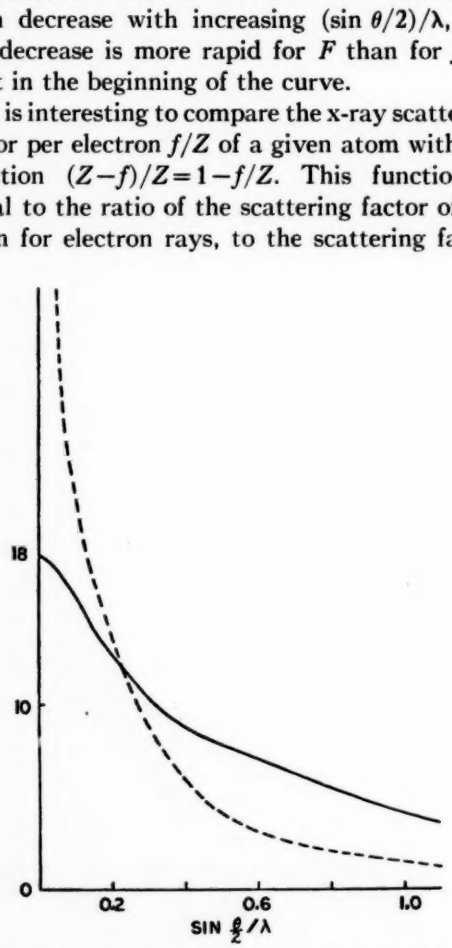

FIG. 1. The atomic scattering factors f and F for the argon atom ($-f$; $----16\pi^2F/10$). f data from J. T. Randall, "The diffraction of X-rays and electrons by amorphous solids, liquids and gases," London, 1934.

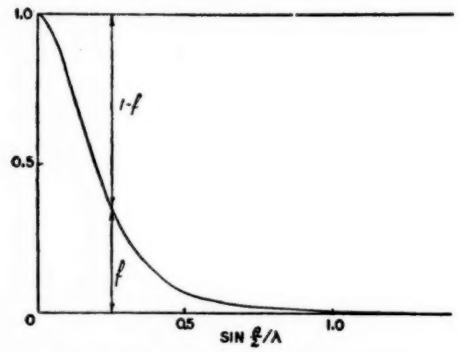

FIG. 2. Functions f and $1-f$ for the hydrogen atom. f data from J. T. Randall (see Fig. 1).

of its naked nucleus; it represents the scattering power per unit of nuclear charge, no account being taken of the factor $k^{-2}s^{-2}$ which is the same for all atoms. For increasing values of $(\sin\theta/2)/\lambda$, destructive interferences in the electronic atmosphere reduce more and more the x-ray scattering power of the atom, which is represented by f/Z, just in the same way as, for electron rays the screening by the electronic atmosphere, which is also represented by f/Z, diminishes. Accordingly, for x-rays, the atom becomes less and less "visible," whereas from a certain point of view, it becomes more and more "visible" for cathode rays. Fig. 2 represents the f and $1-f$ functions for the H atom, $(Z=1)$. When $(\sin\theta/2)/\lambda$ is greater than 1, (λ being measured in A), this atom does not scatter coherent x-ray radiation; for electron rays, on the contrary, its scattering power, the factor $k^{-2}s^{-2}$ being neglected, is at its greatest. It must be emphasized that for heavier atoms this will only occur at much higher values of $(\sin\theta/2)/\lambda$, on account of the greater density of the inner electronic atmosphere, especially of the K shell.

An important point for the study of molecules is the comparison of the scattering factors of different atoms, both for x-rays and electrons. Fig. 3 represents f/Z for several atoms from H to Bi. It shows that the heavier the atom the slower the decrease of f/Z. The light atoms scatter x-rays proportionally less than the heavy ones, and electron rays proportionally more than the heavy ones. Let us examine more closely the case of the atoms C and I, e.g. We shall define for two atoms A and B the ratios

$$K_X(A,B)=f_AZ_B/f_BZ_A \quad \text{(for x-rays)} \qquad (6)$$

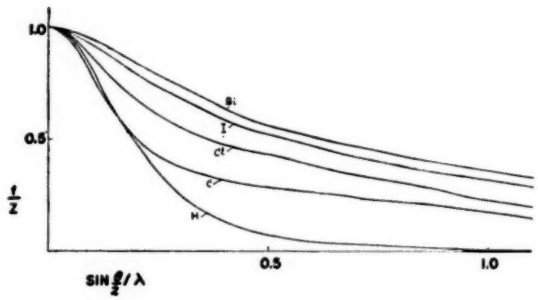

FIG. 3. The scattering power per electron f/Z, for the H, C, Cl, I and Bi atoms. f data from J. T. Randall (see Fig. 1).

and

$$K_E(A, B) = F_A Z_B / F_B Z_A \quad \text{(for electron rays).} \quad (7)$$

These quantities show the importance of the unit scattering power of A relatively to B. The Fig. 4 shows, among other things, that, except at $\theta=0$, where $f=Z$ and $K_X(A, B)=1$, the quantity $K_X(C, I)$ is much less than unity, and on the other hand, that $K_E(C, I)$ is greater than unity. This means that the atomic scattering factors are far from being proportional to their atomic numbers; at $(\sin\theta/2)/\lambda=0.6$, instead of being as 6 and 53, the atomic scattering factors of C and I are for x-rays as 6 and 92, and for electron rays they are as 6 and 39.

In the case of x-rays, the incoherent radiation has an intensity which is zero at $\theta=0$, increases with θ and becomes predominant at large values of $(\sin\theta/2)/\lambda$.[5] For electron rays, it is very large at small angles and it decreases with $(\sin\theta/2)/\lambda$, while the coherent scattering remains important at large values of this variable.[6]

SCATTERING BY MOLECULES

The angular distribution of the mean intensity $\bar{I}$ scattered by a molecule taking all the possible orientations relatively to the primary beam, is given for x-rays by the formula

$$\bar{I} = \frac{I_0}{R^2}\frac{1+\cos^2\theta}{2} a_e^2 \times\left[\sum_i\sum_j f_i f_j \frac{\sin ksl_{ij}}{ksl_{ij}} + \sum_i Z_i G(Z_i)\right] \quad (8)$$

and for electron rays, by the formula

$$\bar{I} = \frac{I_0}{R^2}\frac{4}{a_H^2}\left[\sum_i\sum_j \frac{(Z_i-f_i)(Z_j-f_j)}{k^4 s^4} \times\frac{\sin ksl_{ij}}{ksl_{ij}} + \sum_i \frac{Z_i G(Z_i)}{k^4 s^4}\right]. \quad (9)$$

I_0 is the primary intensity; $(1+\cos^2\theta)/2$ takes into account (for an unpolarized primary beam) the influence of the polarization which is due to the scattering and which reduces the intensity in the neighborhood of $\theta=90°$; l_{ij} is the distance between the ith and the jth atoms in the molecule; the expression $G(Z)$ represents the incoherent scattering function.[6b]

These formulae are extensions of the formula derived in 1915 by Debye[7] for the coherent scattering by a system of *points*, and in which the products of atomic scattering factors were accordingly absent. The use of formulae (8) and (9), where the $\sin x/x$ terms are multiplied by the $f_i f_j$ or $F_i F_j$ products, is only valid on the assumption of molecules constituted of spherically symmetric atoms. In this case, and in this case only, as the scattering factors are then independent of the orientation of the atoms relative to the primary beam, each scattering atom i can be replaced in the calculation by a fictive point, whose scattering power would be different for every diffraction angle θ and is taken equal to f_i or F_i.

Figures 5 and 6 represent the theoretical intensity $\bar{I}$ for the CCl_4 molecule, calculated for

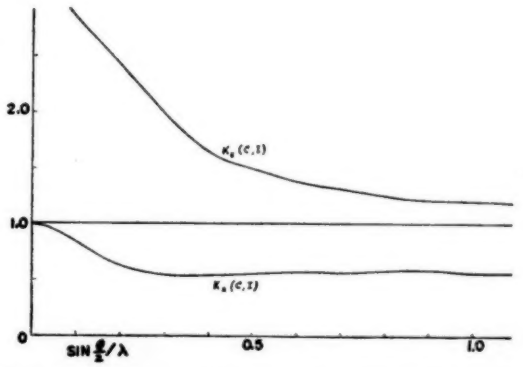

FIG. 4. The importance of the unit scattering power of the C atom relative to the I atom, for x-rays (K_X) and for electrons (K_E).

[5] L. Bewilogua, Physik. Zeits. **32**, 740 (1931).
[6] (a) P. M. Morse, Physik. Zeits. **33**, 443 (1932); (b) L. Bewilogua, Physik. Zeits. **33**, 688 (1932).
[7] P. Debye, Ann. d. Physik **46**, 809 (1915).

both diffraction methods, without the temperature correction, to be discussed later. The curve for x-rays shows five actual maxima, the first ones very well defined. In the curve for electron diffraction, the decrease of intensity is so rapid that, as a rule, inflection points only are observed; however, although being small, the importance of these undulations relative to the background decreases more slowly than in the case of x-rays, because the incoherent intensity does not become

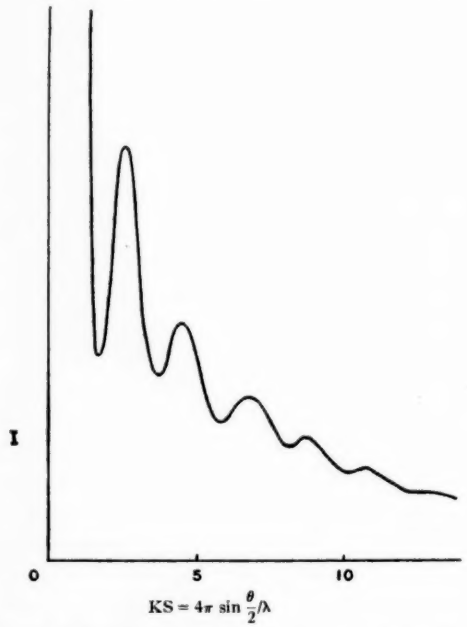

FIG. 5. The mean intensity scattered by the CCl_4 gas for x-rays calculated according to Eq. (8), (without the polarization factor, which cannot be expressed as a function of $(\sin\theta/2)/\lambda$).

of predominant importance at large values of $(\sin\theta/2)/\lambda$.

INFLUENCE OF THE CHEMICAL BOND

As the chemical bond between two atoms is due to a distortion of the electronic atmospheres of these atoms, the use of formulae (8) and (9) involves an error; what does this error amount to? The opinion still exists that it should be important for x-ray diffraction, to the point of making the determination of molecular structures uncertain, while it should be negligible for electron diffraction. As a matter of fact, we will show that the influence of the chemical bond is only appreciable at small values of $(\sin\theta/2)/\lambda$, and moreover that in this special region it is more important for electrons than for x-rays. It is only for very light atoms, like the H atom, that the location of the nucleus of the atom ceases to be possible by the x-ray method, while this is not the case for the electron method.

Debye[1] has pointed out that the contribution of the bonding electrons to the scattering factor f of an atom is appreciable only at very small values of $(\sin\theta/2)/\lambda$, because they are outer electrons and are accordingly distributed in a large and diffuse charge cloud in which important effects of destructive interference occur. In an article on the calculation of f according to Hartree's method, James and Brindley[8] said that, for the same reason, "it is difficult, if not impossible, to distinguish between the different states of ionization of an atom by measuring its f curve." This is strikingly illustrated by a study of aluminum by James, Brindley and Wood, who said: "at all angles of scattering at which spectra can be obtained from the aluminium crystal, the values of f for the different possible states of ionization of the aluminium atom differ by less than the errors of the experimental determination of f."[9] This is shown by Fig. 7, which is reproduced from their paper. In such a case, the influence of the deformation of the outer electronic shells by the chemical bond will evidently be negligible at values of $(\sin\theta/2)/\lambda$ which exceed 0.2.

For small values of $(\sin\theta/2)/\lambda$, the scattering factors f do not differ much from Z, so that the percentage error will be greater in $(Z-f)$ than in f; for example if $f=0.9Z$, one percent difference in f makes ten percent in $(Z-f)$. It follows that, for studying the distribution of the outer electrons, the electron diffraction should be more sensitive than the x-ray diffraction. However, as to the practicability of such investigations, it must be remarked that, if the molecule cannot be represented by a number of spherically symmetric charge distributions, formulae (8) and (9) cannot be used and the calculations become very intricate, as they involve integrations on systems devoid of spherical symmetry.

[8] R. W. James and G. W. Brindley, Phil. Mag. **12**, 81 (1931).

[9] R. W. James, G. W. Brindley and R. G. Wood, Proc. Roy. Soc. **A125**, 401 (1929).

For shorter and shorter wave-lengths, the electron scattering tends towards the "Rutherford scattering," which is due to the nuclei alone. But, if the H atom scatters as a naked nucleus when $(\sin \theta/2)/\lambda$ is one or greater, for heavier atoms this occurs only at much higher values, where measurements would be difficult, because, as we have seen before, if the wave-length is reduced e.g. by a factor 5, the intensity of scattering, according to Eqs. (2) and (3), is reduced by a factor $5^4 = 625$.*

The conclusion is that, under ordinary conditions, the x-rays are actually scattered by the compact inner shells of the atom, which constitute a spherically symmetric system whose center coincides with the position of the nucleus; and the electrons are scattered by the nucleus, account being taken of an important screening due to these inner electron shells. Accordingly no discrepancy is to be expected between the results given by both methods; careful investigations[10] have recently proved this to be the case for CCl_4, where the value 2.86A for the Cl−Cl distances can be considered as exact within limits of error of ±0.01A.[11]

Very light atoms deserve a special treatment. In the H atom, there is no sufficient concentration of electrons around the nucleus to give important x-ray coherent scattering when the influence of the outer part of the atmosphere has become negligible; therefore no hope exists of locating the nucleus by x-ray diffraction. The x-ray diffraction by the molecules H_2O, H_3N, H_4C, which contain the same total nuclear charge, has been studied by Thomer.[12] When $(\sin \theta/2)/\lambda$ is greater than 0.35 they scatter like free O, N or C atoms, the H atoms giving no contribution. At small angles, the x-ray diffraction can be described as due to neon-like, spherical atoms whose atmosphere contains 10 electrons; it is definitely shown that the electronic atmosphere is less concentrated when the number of the nuclei is greater in the molecule.**

What would be the scattering of electrons by such molecules as H_2O? The scattering by the H atoms is important in this case and two approximations to the $(Z-f)$ factors can be made: either we consider the three atoms as surrounded by the atmospheres they would have if they were free (approximation I), or we consider two naked H nuclei and a neon-like central atom according to Thomer (approximation II). The Fig. 8 gives $K_E(H, O)$ (formula 7) according to approximations I and II. When $(\sin \theta/2)/\lambda$ is less than 0.4, the difference between I and II is very great, this region should be used for studying the chemical bond. Beyond 0.8, I and II are practically the same; the K electrons of the O atom are the only ones still

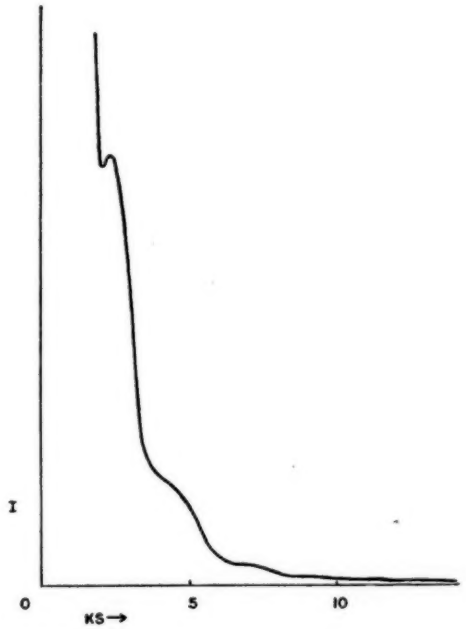

FIG. 6. The mean intensity scattered by the CCl_4 gas for electrons, calculated according to Eq. (9).

scattering effectively. Between 0.4 and 0.8 the differences are not very important; as it is improbable that no electron screening remains

* Moreover, in this region the undulations of $\sin x/x$ become less and less important, and they are further reduced on account of the thermal movements in the molecule.

[10] C. Degard, J. Piérard and W. van der Grinten, Nature **136**, 142 (1935).

[11] P. Debye, *Nobelvortrag* (Stockholm, 1937).

[12] G. Thomer, Physik. Zeits. **38**, 48 (1937).

** The neon-like representation is in agreement with experiment, but it is not certain that it is perfectly exact, because different electronic distributions can always be imagined which would give the same mean scattered intensity. Supplementary assumptions are necessary for determining the molecular structure. However in ordinary cases where the difficulty of the chemical bond can be disposed of, these assumptions are scarcely open to discussion: they amount to considering the chlorine gas e.g. as constituted of Cl_2 molecules, where each Cl atom has an electron distribution to be calculated, for instance, according to Hartree.

around the H nuclei in this region, the approximation II is certainly an exaggeration and one can have considerable confidence in approximation I. Accordingly the measurements will be possible when $(\sin \theta/2)/\lambda$ is 0.4 or greater, with the use of ordinary scattering factors for the calculations. It should be noted that $K_E(H, O)$ is still some fifteen percent greater than unity at $(\sin \theta/2)/\lambda = 1.4$, i.e., in the outer part of the diffraction patterns which are usually obtained. Of course these considerations are valid not only for molecules like H_2O, but also for any complicated molecules like CH_3CH_2Cl; and the calculations can be made with formula (9), i.e., with the use of the scattering factors F defined by formula (5) for all atoms, with the condition that no consideration should be given to measurements at small diffraction angles. According to Thomer[12] the x-ray scattering by the groups CH_3, NH_2, OH, etc., can be taken into account at small diffraction angles by assuming that they are constituted of spherically symmetric electronic atmospheres. But, even if the atmosphere is spherical, it is evidently not symmetric around the H nuclei and no scattering factors for electrons can be calculated for the H atom on these grounds. Thus the study of molecules containing H atoms is possible at smaller diffraction angles in x-ray than in electron diffraction.*

The Location of Light Atoms in Molecules Containing Both Light and Heavy Atoms

Every interatomic distance in a molecule gives rise to a fluctuating intensity term in formula (8) or (9). Let us first examine the most simple case, that of a diatomic molecule built of the atoms 1 and 2, at a distance l apart. For x-rays, the coherent intensity will be proportional to

$$f_1^2+f_2^2+2f_1f_2(\sin ksl)/ksl.$$

This formula shows that the greater the distance l the more numerous the fluctuations in the angular distribution of the intensity, and also that the slower the decrease of the factors f_1 and f_2 with the scattering angle the sharper the maxima will be. See P. Debye.[1] It follows that a molecule like F_2, where the electronic atmospheres are not very concentrated and where the distance F−F is small, will give much less favorable patterns than Br_2, where the distance Br−Br is greater and where the electronic atmospheres are more concentrated. But it should be borne in mind that the important quantity which occurs in the formula is the product f_1f_2, not the factors f_1 and f_2 taken separately, so that a molecule like ICl will probably give nearly as good a pattern as Br_2, although it contains an atom (Cl) three times lighter than the other (I). It is evident, however, that if one of the atoms has a scattering factor which becomes vanishingly small where the influence of the chemical bond is negligible, as it would be the case for HBr, the measurement is impossible by x-ray diffraction. On the contrary, the measurement of the H−Br distance by electron diffraction remains possible, since the scattering by the H atom is important in this case.

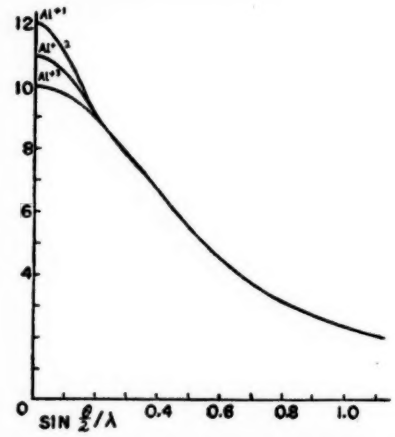

Fig. 7. Atomic scattering factors f calculated for the Al^{+1}, Al^{+2} and Al^{+3} ions. (See reference 9.)

In polyatomic molecules, the importance of each distance l_{ij} is given by the product f_if_j or F_iF_j. Distances between heavy and heavy, between heavy and light, between light and light atoms are of decreasing importance. As examples of molecules containing atoms of different weights, let us discuss the case of the chloromethanes. In the electron investigation of the molecule CH_3Cl the H−H distances are not important but the three H−Cl distances are by

* Inner rings are often discarded as unreliable in electron diffraction work.

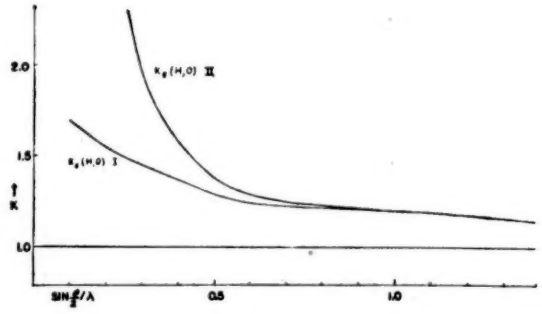

FIG. 8.

no means negligible; the factor

$$3F_H F_{Cl}/F_C F_{Cl} = 3(1-f_H)/(6-f_C),$$

which gives their importance relative to that of the C−Cl distance, is $3\times 0.96/4.6 = 0.64$ for $(\sin\theta/2)/\lambda = 0.6$. Moreover the undulations due to these H−Cl distances will be relatively sharp, since they are longer than the C−Cl distance. The conclusion is that the C−Cl value depends appreciably on the assumption which has to be made on the position of the H atoms because the parameters are too numerous to be all easily determined by electron diffraction only. But under suitable conditions the H atoms are invisible in the x-ray method, which will then give with certainty the C−Cl distance, the only parameter left in this case. Once the C−Cl distance is known, precise electron measurements could locate the H atoms.

For x-ray diffraction, the molecule CH_2Cl_2 can be considered as a CCl_2 group with two C−Cl distances whose importance, relative to the Cl−Cl distance, is $2f_C f_{Cl}/f_{Cl}^2 = 0.5$. This is more favorable to the determination of the Cl−C−Cl angle than in the case of $CHCl_3$, where the three C−Cl distances have, relative to the three Cl−Cl distances, an importance equal to 0.25; as for CCl_4, the importance of the four CCl relative to the six Cl−Cl is only 0.17, (in each case for $(\sin\theta/2)/\lambda = 0.6$). This shows that the presence of heavy atoms is not sufficient to render uncertain the location of the light atoms in a molecule; it is only so when the heavy atoms are in such number as to have between themselves distances which are of predominant importance. Far from being unfavorable, the presence of one heavy atom in a molecule will, on the contrary, emphasize the position of the light ones, as e.g. the Cl atom in CH_3Cl, $CH_2=CHCl$, etc.

Once the C−Cl and Cl−Cl distances are measured by x-rays in CH_2Cl_2, the electron investigation will give indications as to the position of the H atoms; here we have one Cl−Cl, two C−Cl and four Cl−H distances, whose importance is respectively 1, 0.84 and 0.36. In $CHCl_3$ the importance of the three Cl−Cl, the three C−Cl and the three Cl−H distances will be 1, 0.42 and 0.09; the location of the H atom is scarcely possible; conversely, the fact of assuming the position of the H atom does not matter much here.

It follows that the structure of the molecules CH_3Cl and CH_2Cl_2 could probably be entirely determined by diffraction methods without arbitrary assumptions (except, perhaps, on the symmetry of the molecule). This could only be achieved by the use of both x-ray and electron methods, each of them alone being insufficient. In the $CHCl_3$ molecule the location of the H atom is scarcely possible, and the location of the C atom is less easy than in the CH_2Cl_2 molecule. In the CCl_4 molecule the location of the C atom is still less easy. This discussion shows that the precision of the interatomic distance measurements must be critically examined in each particular case, as the same atom may be easy to locate in one molecule, and difficult in another molecule.

THERMAL MOVEMENTS IN THE MOLECULES

The existence of thermal movements inside the molecule is not to be overlooked when determining molecular structures by diffraction methods. We are not dealing with rigid and identical molecules, and instead of calculating the scattered intensity by introducing constant distances l_{ij} in formulae (8) and (9), we should evaluate the mean intensity which is scattered by a number of molecules where the interatomic distances vary continually. The effects of the vibrations in diatomic and regular tetrahedral molecules has been theoretically investigated by James,[13] they can be accounted for by multiplying the products $f_i f_j$ or $F_i F_j$ (where $i \neq j$), in

[13] R. W. James, Physik. Zeits. **33**, 737 (1932).

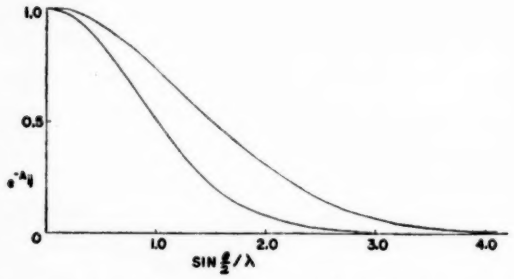

FIG. 9. The factors $e^{-A_{ij}}$ for the CCl_4 molecule at 300°C. For the C−Cl distances, $((\delta l_{C-Cl}^2)_{Av})^{\frac{1}{2}}=0.062$A and for the Cl−Cl distances, $[(\delta l_{Cl-Cl}^2)_{Av}]^{\frac{1}{2}}=0.092$A. It is interesting to note that at 0°C, these quantities are still respectively 0.056A and 0.076A, and at the absolute zero, 0.051A and 0.054A.

formulae (8) or (9), by a factor $e^{-A_{ij}}$, A_{ij} being given by the formula

$$A_{ij}=8\pi^2(\delta l_{ij}^2)_{Av}[(\sin\theta/2)/\lambda]^2,$$

where $(\delta l_{ij}^2)_{Av}$ is the mean square of the variation of the distance l_{ij}. The difficult calculation of the $(\delta l^2)_{Av}$ has not been extended to other types of molecules.

In x-ray investigations of the molecules $SiCl_4$[13] and CCl_4[14] the influence of thermal vibrations was too small to be detected, and this agreed with the theory; Fig. 9 shows that the correction factors $e^{-A_{ij}}$, up to $(\sin\theta/2)/\lambda=0.6$, which is the limit of the measurements, are not very different from unity. Afterwards the decrease is more rapid and, actually, in an electron investigation of CCl_4,[10, 15] the temperature correction was necessary for bringing agreement between calculation and observation at the fifth apparent maximum. It follows that this influence is certainly appreciable in the range of $(\sin\theta/2)/\lambda$ which is covered by many electron measurements (up to $(\sin\theta/2)/\lambda=1.4$; tenth "maximum"). The temperature correction had no effect on the distance measurements in CCl_4 which we have quoted above, but there the Cl−Cl distance, of predominant importance, was practically the only one to be measured. In such a case the position of the maxima is little affected by the temperature correction and is more important than their intensity for determining the distance.

[14] W. van der Grinten, Physik. Zeits. **34**, 609 (1933).

[15] C. Degard and W. van der Grinten, Bull. Soc. Sc. Liège, Nos. 4–5 (1935); Second Congrés Nat. Sci., Bruxelles 1935, p. 563. See M. Camus and C. Degard, Bull. Soc. Sc. Liège, Nos. 8–10 (1937) for a study of $SiCl_4$.

In molecules with several kinds of interatomic distances of comparable importance, the influence of thermal vibrations may be different for the different distances and it has not been proved that the correction will not notably alter the appearance of the diffraction curves.

According to James' calculations, at still higher values of $(\sin\theta/2)/\lambda$, the importance of the undulations will be drastically reduced: the Cl−Cl interferences in CCl_4 at 300°C for $(\sin\theta/2)/\lambda=2.0$ by a factor 0.08, for $(\sin\theta/2)/\lambda=3.0$ by a factor 0.002. This may prove disturbing for measurements of interatomic distances, but on the other hand, it could be used for studying the vibrations in the molecule, because the angle at which the intensity undulations for a given interatomic distance l_{ij} become vanishingly small depends on the value of the mean square variation $(\delta l_{ij}^2)_{Av}$ of this distance, as Fig. 9 shows for the two distances in CCl_4.* X-ray measurements have little interest in this region of high $(\sin\theta/2)/\lambda$, on account of the importance there of the incoherent, relatively to the coherent, intensity; nevertheless, even under ordinary conditions, no important increase of precision will probably be obtained without taking into account the temperature correction. Moreover, as the quantities $[(\delta l_{ij}^2)_{Av}]^{\frac{1}{2}}$ are of the order of magnitude of 0.05A or 0.10A, it is to be questioned if attempts to get a precision appreciably greater than 0.01A, say, 0.001A, will not be meaningless.

The study of molecules with rotating groups, like CH_2Cl-CH_2Cl, has been made by x-ray diffraction[16] and also by electron diffraction.[17] As this constitutes a less general problem than the problem of vibrations, we refer to the original papers.

THE PRESENT STATE OF THE X-RAY DIFFRACTION TECHNIQUE

Let us examine the experimental possibilities of the x-ray method by a discussion of the in-

* Figure 9 shows that, at values of $(\sin\theta/2)/\lambda$ greater than 2.6, the C−Cl undulations constitute practically the whole diffraction pattern; hence a possible method of measuring individually certain distances in the molecules.

[16] F. Ehrhardt, Physik. Zeits. **33**, 605 (1932); H. Berger, Physik. Zeits. **38**, 370 (1937).

[17] J. Y. Beach and K. T. Palmer, J. Chem. Phys. **6**, 639 (1938).

vestigation we have carried out of the silicochloroform molecule $SiHCl_3$.* This study was undertaken in order to obtain a direct and accurate measure of the valency angle in a chloroform-like molecule. The $SiHCl_3$ molecule has characteristics which answer this purpose, for the three Si−Cl distances are of about the same importance in it as the three Cl−Cl distances, and both Si and Cl atoms have concentrated electronic atmospheres.

Since there are two kinds of distances in the molecule, exact intensity measurements were necessary. This implied monochromatic measurements. Van der Grinten[14] showed that the diffraction of crystal-reflected x-rays by the CCl_4 gas gives intensity curves in remarkable agreement with the theory. That this is not to be expected when not strictly monochromatic radiation is used, is shown by Figs. 10 and 11. Comparison of the microphotometer records of x-ray diffraction patterns of $SiHCl_3$ taken with crystal-reflected and with filtered radiation shows definitely the deficiency of the last technique; in the case of filtered radiation no trace is left of the second minimum and maximum except an inflection in the curve.

The drawback of the use of crystal-reflected x-rays is the lengthening of the times of exposures which in some investigations have exceeded 100 hours. A diminution of these times of exposure is necessary for the method to become of practical use. As a matter of fact, the use, in the investigation already referred to, of an apparatus working with gas under some four atmospheres has achieved a threefold increase in the scattered intensity.** Good photographs have been obtained in eight hours, and in 35 hours very dark photographs, which would have required 100 hours with the old technique. The microphotometer record reproduced in Fig. 10 is the record of a photograph taken in somewhat less than eight hours. The second and the third maxima, which are the most important part of the pattern, can be readily measured on this record. The construction of the diffraction chamber is such that the first maximum does not appear in the photograph, but a modified apparatus would give the most intense first maximum together with the second maximum twice as rapidly, i.e., in only four hours.

Intensity marks made with a rotating sector allow an easy determination of the experimental intensities as a function of the scattering angle. This experimental curve is compared with theoretical ones calculated for different $SiCl_3$ models, these calculations involving all corrections for absorption, scattering volume etc., so as to allow a complete comparison with the measured curve. The greater part of the discussion is based on an analysis of the second and third maxima and minima. It may seem at first sight that these data constitute a less significant basis for discussion than the numerous "maxima" available in the electron diffraction. But it must be borne in mind that the x-ray data are objectively and accurately measured by the microphotometer, especially the position of the maxima and minima which is even independent of the law of blackening of the film.† However the other bumps in

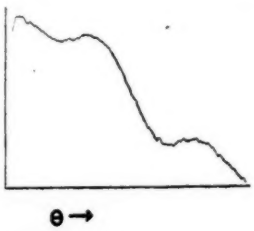

FIG. 10. Trace of a microphotometer record of a diffraction pattern of $SiHCl_3$ made in 7 hours 40 min. with rocksalt-reflected molybdenum $K\alpha$-radiation. The maxima are situated at about $\theta=25°$ and $\theta=41°$, respectively.

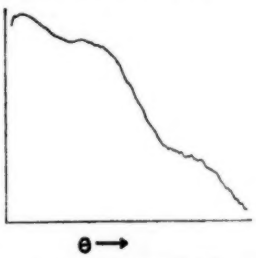

FIG. 11. Trace of a microphotometer record of a diffraction pattern made in 15 minutes with molybdenum $K\alpha$-radiation filtered through a zirconium foil.

* M. H. Pirenne, Comptes rendus **206**, 516 (1938). Full details will appear in *Physikalische Zeitschrift*.

** Apparatus have been built on the same principle already, but they give an intensity increase of only about fifty percent. (E. O. Wollan, Phys. Rev. **37**, 862 (1931); G. Herzog, Helv. Phys. Acta **6**, 508 (1933).)

† Besides, proof was incidentally obtained that only two maxima and minima are sufficient to give a reliable set of data. At first an error of about one degree was left unnoticed in the measurement of the scattering angles; with this error agreement was impossible with any of the numerous $SiCl_3$ models which were put to trial, even for the positions of the maxima and minima.

the curve are also given due consideration in the discussion. Quantitative comparison of the intensities of the maxima and minima allows a determination of the valency angle independent to a certain extent of the determination of the absolute dimensions of the molecules.* The following values were found for the dimensions of the molecule:

$$Cl-Cl=3.27\pm0.03A;\quad Si-Cl=1.98\pm0.02A;$$
$$Cl-Si-Cl=111.5\pm1°.$$

By analogy with the case of $SiCl_4$, it was inferred that the influence of the thermal vibrations, to which the measurement of the valency angle would be especially sensitive, is less than the given experimental errors. Two electron investigations have been made on $SiHCl_3$. De Hemptinne and Wouters[18] found:

$$Cl-Cl=3.39A;\quad Si-Cl=2.05A;$$
$$Cl-Si-Cl=111°\pm4°;$$

and Brockway and Beach:[19]

$$Cl-Cl=3.29\pm0.03A;\quad Si-Cl=2.01\pm0.03A;$$
$$Cl-Si-Cl=110°\pm1°.$$

There is a discrepancy between the distance values of the first investigation and the x-ray values. On the other hand, the results of the second investigation agree with the x-ray values within the given limits of error. However, the electron investigation tends to indicate a smaller Cl−Si−Cl angle; we would suggest that the neglecting of the temperature effect in the electron investigation accounts perhaps for this difference, as some of the maxima which have been especially examined for determining the valency angle (3rd, 4th, 8th and 9th) must be sensitive to the temperature effect.

Let us say something of the prospects of development of the x-ray technique. New, more effective, intensifying screens provide a means of diminishing the times of exposure. X-ray tubes with rotating anodes which are now being developed, will give a much greater primary intensity than the tubes now available. Accordingly it is not presumptuous to assert that it will soon be possible to make diffraction photographs in one or two hours with crystal-reflected x-rays. Furthermore, another possibility is open; the use of balanced filters[20] in photographic or ionometric measurements; this method yields monochromatic results from the difference taken between measurements made with filtered radiation, and we have seen that the times of exposure are measured in minutes when filtered radiation is used. The use of Geiger-Müller counters may also prove helpful in the study of x-ray diffraction by gases.[21]

No group of workers has undertaken systematic investigations by the x-ray diffraction technique for a large number of molecules as has been the case with the electron diffraction technique. We should say that the lack of reliable x-ray data is not due to the defects of the x-ray method but to the neglect this method has suffered.

Conclusion

X-ray diffraction by gas molecules easily gives intensity of scattering curves. As a rule, these curves show actual maxima and minima, which are the most prominent just where the effect of molecular vibrations is the smallest. In practice, the times of exposure are on the way to being reduced to convenient periods. Electron diffraction, in very short times of exposure, gives more maxima than x-ray diffraction, and the outer maxima have the advantage of being more sensitive to changes in the molecular parameters. But these undulations are much less well defined, and reliable intensity curves are difficult to obtain. Moreover, the temperature correction is important for the maxima of a higher order than those usually obtained by x-ray diffraction, but is unfortunately difficult to calculate. For these reasons, when intensities are important, as for the study of valency angles or intramolecular rotation, x-ray diffraction may afford a superior treatment. The first part of this article has shown, however, that the location of the H nuclei requires the use of electron diffraction, but, on the other hand, the treatment of mole-

* For all details see the article in *Physikalische Zeitschrift.*

[18] M. De Hemptinne and J. Wouters, Nature **138**, 884 (1936); **139**, 928 (1937).

[19] L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc. **60**, 1836 (1938).

[20] P. A. Ross, J. Opt. Soc. Am. **16**, 433 (1928).

[21] W. van der Grinten and H. Brasseur, Nature **137**, 657 (1936); also P. Ohlin, Physik. Zeits. **39**, 567 (1938).

cules containing H atoms is simpler by x-ray diffraction. In all cases where accuracy is desired, parallel investigation by both diffraction methods is advisable.*

ACKNOWLEDGMENTS

I should like to express my thanks to Professor P. Debye for his assistance and for his generous hospitality in the Kaiser Wilhelm-Institut für Physik, Berlin-Dahlem, where the writing of this article was begun. I am also indebted to Dr. J. Y. Beach of the Frick Chemical Laboratory for valuable discussions.†

* An extensive treatment of the subject of the diffraction of x-rays by gases, including the comparison with electron diffraction, will be published in *Actualités scientifiques et industrielles* (Hermann editor, Paris).

† *Note added in proof.* A preliminary communication of P. P. Debye (Physik. Zeits. **40**, 66 (1939)) shows that it is possible to obtain actual maxima in electron diffraction photographs, by a device consisting of a rotating sector which suppresses the influence of the factor s^{-4} of Eq. (9). The principal disadvantage of electron diffraction is in this way removed and a number of points of the above discussion will have to be reconsidered in the future; but this discussion remains valid for the results obtained up to now. The new technique is especially valuable for the location of light atoms and for the study of thermal movements in molecules.

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Some Chemical Properties of Element 43. II

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*Palermo, Italy**

(Received January 10, 1939)

IN A previous paper of the same title[1] we have given some results of a chemical investigation of a radioactive isotope of element 43. Thanks to Professor E. O. Lawrence who has supplied us with more of the radioactive material, the investigation has been extended, and we give the results here.

We have found a very simple method for extracting the activity, i.e., the element 43, from the bombarded molybdenum. Since the activity is confined to a very thin layer, determined by the range of the deuterons in the molybdenum target, it is sufficient to attack only the surface of the molybdenum in order to carry the activity into solution. The simplest way for doing this is to boil the molybdenum in ammonium hydroxide after addition of a small amount of hydrogen peroxide. In some hours it is possible to extract in this way a large fraction of the active material mixed with only a few milligrams of molybdenum. Particularly, one has the 43 free from rhenium, the necessary presence of which was an unpleasant feature of the method previously used.

We have checked again the separations from Mo, Cb and Zr and for all the three elements less than one percent of the activity was found with the Mo, Cb or Zr fraction.

For the separation from molybdenum we have found it preferable in some cases to precipitate the molybdenum with 8-hydroxiquinoline, and then acidify the filtrate and precipitate the 43 with hydrogen sulfide from an hydrochloric solution using rhenium as a carrier, rather than to precipitate the molybdenum with 8-hydroxiquinoline and the 43 with nitron (diphenyl-endo-anilo-hydro-triazole). In this way it is possible to perform a quantitative separation of the two elements in two to three hours.

SULFIDES

We have investigated in a more quantitative way the precipitation of element 43 as a sulfide. In hydrochloric acid solution from 0.4 to 5 normal, using a few milligrams of platinum or rhenium as a carrier, the precipitation after 24 hours is complete. With 10 normal hydrochloric acid only a very small fraction of the total amount of 43 precipitates, whereas rhenium precipitates with a good yield, though slowly;

* Now at the Radiation Laboratory, University of California.

[1] C. Perrier and E. Segrè, J. Chem. Phys. **5**, 715 (1937).

similar results were obtained using arsenic as a carrier. We think that this property could be used for a fractional separation of 43 from rhenium or from other elements which precipitate with hydrogen sulfide even in very acid solution.

In an alkaline ammonia solution we have used manganese iron and zinc as carriers. The precipitation with manganese seems to be fairly complete, somewhat less complete with iron and even less (order of magnitude of 25 percent) with zinc.

Fractional Crystallization

Considering the possibility of a separation by fractional crystallization of rhenium and 43, we have tried to determine the partition coefficient of 43 between a solution of potassium perrhenate and crystals of the same compound. The measurements were made by adding to a potassium perrhenate solution a known amount of a solution containing 43, very probably in its highest stable state of oxidation. The mixture was partially evaporated at the constant temperature of 14°C and the activity of the crystals and of the residue measured. As a mean value of several measurements we have found a partition coefficient of the specific activity (activity per mg of substance) between the solution and the solid of 2.6. However, individual measurements gave results varying between 3.7 and 2.2. These large variations are mainly due to difficulties in the measurement of the very soft β-radiation by which the activity is detected.

Similar measurements on caesium perrhenate and 43 gave a partition coefficient between the solution and the solid salt of 0.75.

We have also tried to see if there was an appreciable partition between nitron perrhenate and the corresponding 43 salt; however the nitron perrhenate carried all the activity; in fact adding rhenium we obtained a second precipitation of nitron perrhenate which carried less than one percent of the activity.

Ether Extraction

We have extracted molybdenum from our 43 samples, with ether, by first oxidizing the 43 with chlorine and then shaking the solution to which potassium sulfocyanide and hydrochloric acid had been added, with ether.[2] Only a small amount of 43 went into the ether.

Electrolysis

It has been possible to prepare extremely thin layers of 43 by electrolytic deposition on platinum by a process used by Hoelemann for rhenium.[3] These layers are possibly metallic and they evaporate completely by heating to 300°C in air. This result should be compared with our previous observations on the volatility.[1]

Volatility

We have precipitated from an hydrochloric acid solution 10 mg of rhenium, 10 mg of platinum and a certain amount of 43. The sulfides have been heated at 100°C in a current of chlorine. The chlorine was not specially dried. Rhenium sulfide and the active material volatilized completely and were partially collected in the cold parts of the tube.

Reduction

An alkaline solution containing bismuth, potassium perrhenate and 43 was treated with stannous chloride. The bismuth precipitate does not carry the activity if it is separated immediately but absorbs it on long standing. This result should be compared with the behavior of rhenium which does not precipitate in alkaline solution by reduction with stannous chloride.

We wish to thank Professor E. O. Lawrence and the Radiation Laboratory of the University of California for their gift of the bombarded molybdenum which made this investigation possible.

[2] E. Einecke, Zeits. f. analyt. Chemie **90**, 220 (1932).
[3] H. Hoelemann, Zeits. f. anorg. Chemie **211**, 195 (1933).

Van der Waals' Forces and the Vapor Pressures of Ortho- and Parahydrogen and Ortho- and Paradeuterium*

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The nonexchange interaction energies of pairs of orthohydrogen and of parahydrogen molecules are examined in detail. The first-order contribution is seen to contribute the specific heat anomaly of *o*-hydrogen at low temperatures. The second-order interaction is computed for cases where the first-order contribution is zero. Its contribution, calculated with explicit recognition of the influence of rotational energy on the electronic states, is shown to be of the correct sign and order of magnitude to account for the vapor pressure and volume differences of *o*- and *p*-hydrogen and deuterium. More exact confirmation cannot be obtained because of the approximations and the disturbing influence of the anharmonic zero-point vibrations.

1. INTRODUCTION

THE isolation of ortho and para forms of two hydrogen isotopes has given us data on the properties of simple solids and liquids, and has at the same time revealed our inability to treat molecular solids theoretically. Before embarking on the fundamental task of devising a theory of molecular solids we are confronted with certain disturbing auxiliary phenomena; among these are the vapor pressure differences of the ortho and para forms, and the anomalous specific heat of orthohydrogen (paradeuterium). The "auxiliary" effects cannot be completely removed without solving the main problem, but by attacking the smaller problems first, one may hope to gain an insight into certain aspects of the main problem, such as, for example, the property of rotation in solids.

This paper will examine the contribution of the van der Waals-London forces to the vapor pressure differences of the ortho and para forms of the hydrogens. We will first eliminate the freezing out of the degeneracy of the orthohydrogen molecules as a possible cause of the vapor pressure difference.

The vapor pressure of solid hydrogen is, for parahydrogen[1]

$$\ln p=-\frac{\chi_p}{RT}+\ln\frac{(2\pi m)^{3/2}(kT)^{5/2}}{h^3}+\frac{A}{V}\left(1+\frac{B}{T^2}\right)+\frac{pV_s}{RT}-\int_0^T\frac{dT}{RT^2}\int_0^T C_{p=0}dT, \quad (1)$$

and for orthohydrogen

$$\ln p=-\frac{\chi_0}{RT}+\ln 3+\ln\frac{(2\pi m)^{3/2}(kT)^{5/2}}{h^3}+\frac{A}{V}\left(1+\frac{B}{T^2}\right)+\frac{pV_s}{RT}-\int_0^T\frac{dT}{RT^2}\int_0^T C_{p=0}dT-\int_0^T\frac{dT}{RT^2}\int_0^T C_{p=0}^{(a)}dT-\frac{1}{RT}\int_0^T C_{p=0}^{(a)}dT, \quad (2)$$

where $C_{p=0}$ is the specific heat at zero pressure of parahydrogen, $C_{p=0}^{(a)}$ is the "anomalous" specific heat of orthohydrogen, χ_p is the molar heat of vaporization of p-H_2 at 0°K, and χ_0 represents the molar heat of vaporization of o-H_2 at 0°K, considered as freely rotating and 3^N-tuply degenerate.

If at $T=T_1$, $C_{p=0}^{(a)}=0$, then for $T>T_1$ the last two terms of (2) give $-\Delta S$ (mixing) $=-\ln 3$, and (2) falls immediately into the form (1). If $C_{p=0}^{(a)}<K$ at some temperature T_1, and $C_{p=0}^{(a)}=0$ for $T=T_2>T_1$, then at any temperature $T(T_1<T<T_2)$ the contribution to $\ln p$ is less than

$$\frac{K}{R}\left\{1-\frac{T_2}{T}+\ln\frac{T_2}{T}\right\}.$$

The data of F. Simon *et al.*[2] allow us to assert safely that $T_2=20$°K, and that for $T_1=12°$, $K=0.05$; hence a contribution to p of less than 0.1 percent. The vapor pressure difference of *o*-

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[1] R. B. Scott, F. G. Brickwedde, H. C. Urey and M. H. Wahl, J. Chem. Phys. **2**, 454 (1934).

[2] K. Mendelssohn, M. Ruhemann and F. Simon, Zeits. f. physik. Chemie **B15**, 121 (1931).

and p-H_2 is of the order of 5 percent.[3, 4] We conclude that the removal of the 3^N-fold degeneracy of the ortho state is not responsible for the observed difference in vapor pressure.[5]

2. The van der Waals-London Energies

We are to calculate the interaction energies of two orthohydrogen or of two parahydrogen[5] molecules, at distances such that the probability of electron interchange is small, and on the assumption that the lowest energy state remains degenerate. If V be the Coulombic interaction energy, we find on expansion in inverse powers of the intermolecular distance r

$$V=\sum_{i=1}^{4}V_i=-\frac{\mu_1\mu_2}{r^3}P_1+\frac{3}{2}\frac{\mu_1\tau_2}{r^4}P_2$$
$$+\frac{3}{2}\frac{\mu_2\tau_1}{r^4}P_3+\frac{3}{4}\frac{\tau_1\tau_2}{r^5}P_4+\cdots=\sum_{i=1}^{4}V_{i0}P_i, \quad (3)$$

where μ_1, τ_1 are the (instantaneous) dipole and quadrupole moments of the first molecule; μ_2, τ_2 the corresponding quantities for the second.

Now, the first-order interaction energy is the average of the roots of the determinantal equation

$$|(H_0'\beta'|V|H_0\beta'')-\delta_{\beta'\beta''}\varepsilon|=0, \quad (4)$$

and the second-order interaction is[6]

$$\varepsilon^{(2)}=\frac{1}{D}\sum_{\beta'}\sum_{H_0''\beta''}{}'$$
$$\times\frac{(H_0'\beta'|V|H_0''\beta'')(H_0''\beta''|V|H_0'\beta')}{H_0'-H_0''}, \quad (5)$$

provided that

$$|H_0'-H_0''|\gg(H_0'\beta'|V|H_0''\beta''). \quad (6)$$

In the above equations $(H_0'\beta'|V|H_0''\beta'')$ is the matrix element referring to the β'th unperturbed degenerate state of energy H_0' of the two molecules (taken as a single system), and the β''th degenerate state of energy H_0''; D is the degree of degeneracy of the ground (H_0') state.

Since the maximum value of

$$\frac{(H_0'\beta'|V|H_0''\beta'')}{|H_0'-H_0''|}\sim\frac{\tau^2}{r^5}\cdot\frac{4\pi^2I}{h^2}$$

(where τ, the permanent quadrupole moment of H_2, $=0.580\times10^{-26}$ e.s.u.[7], $r=3.55$A[8] and I is the moment of inertia of one of the molecules) $=0.026$ for H_2 and 0.051 for D_2, condition (6) is fulfilled.

For pairs of parahydrogen molecules, the one root of (4) is zero: for pairs of orthohydrogen molecules,[5] the sum of the roots of the 3×3-rowed matrix is zero. The latter result is full of physical significance. The various roots, proportional to τ^2/r^5 represent the *orientational eigenstates of the rotating ortho molecule pair:* if the crystal of $N/2$ pairs did not present a cooperative phenomenon—as the properties of the eigenfunctions show it must—these roots would give us immediately the energy levels of the orientational degeneracy of crystalline orthohydrogen, and, hence, allow us to compute directly the associated "anomalous" specific heat. We can easily verify, disregarding the cooperative aspects of the phenomenon, that the energies of interaction of the permanent quadrupoles are of the same order of magnitude as the freezing-out energy. The fact that the sum of the roots of (4) is zero is then the mathematical equivalent of our assumption that the orientational degeneracy is unremoved.[9]

We will first evaluate (5) assuming that

$$H_0''=H_1''+H_2''=H_{A1}''+j_1''(j_1''+1)\frac{h^2}{8\pi^2I}$$
$$+H_{A2}''+j_2''(j_2''+1)\frac{h^2}{8\pi^2I}$$
$$=H_{A1}''+j_1''(j_1''+1)Q$$
$$+H_{A2}''+j_2''(j_2''+1)Q,$$

[3] W. Keesom, A. Bijl and H. van der Horst, Leiden Communication No. 217a (1931).

[4] F. G. Brickwedde, R. B. Scott and H. S. Taylor, J. Chem. Phys. **3**, 653 (1935).

[5] The corresponding results for pairs of paradeuterium molecules and of orthodeuterium molecules are obtained here, as throughout, by changing the words "orthohydrogen" for "paradeuterium," etc.

[6] J. E. Lennard-Jones, Proc. Roy. Soc. **A129**, 598 (1930).

[7] Calculated from H. M. James and A. S. Coolidge, Astrophys. J. **87**[4], 438 (1938).

[8] The minimum distance between 2 molecules, assuming a face-centered cubic lattice is, for H_2: $r=3.789$A ($V=23.31$ cm^3); for D_2: $r=3.628$A ($V=20.48$ cm^3); $r=3.55$A corresponds to a vibrationless lattice.

[9] It is proposed to present a detailed treatment of the orientational degeneracy in a subsequent paper.

where H_{A1}'' is the energy of one molecule for $j_1''=0$, and $j_1''(j_1''+1)Q$ ($j_1''=0, 1, 2\cdots$) is the rotational energy. This assumption (that the electronic and vibrational levels are independent of rotational energy) will be dropped later. Then

$$(H_0'\beta'|V|H_0''\beta'') = \sum_{i=1}^{4}(H_{A1}'H_{A2}'|V_{i0}|H_{A1}''H_{A2}'') \times (j_1'j_2'\beta'|P_i|j_1''j_2''\beta''). \quad (7)$$

The matrix elements of the P_i might equally well be written

$$(j_1'j_2'm_1'm_2'|P_i|j_1''j_2''m_1''m_2'') \text{ with } m_i'=0, \pm 1;$$

this gives the significance of the β''s. From (7) and the selection rules for dipole and quadrupole transitions we find that

$$(H_0'\beta'|V_i|H_0''\beta'')(H_0''\beta''|V_j|H_0'\beta')=0$$

unless $i=j$; hence,

$$\varepsilon^{(2)}=\sum_{i=1}^{4}\frac{1}{D}\sum_{\beta'\beta''}\sum_{H_A''j''}{}' \times\frac{|(H_{A1}'H_{A2}'|V_{i0}|H_{A1}''H_{A2}'')|^2|(j_1'j_2'\beta'|P_i|j_1''j_2''\beta'')|^2}{H_{A1}'+H_{A2}'-H_{A1}''-H_{A2}''+\{j_1'(j_1'+1)+j_2'(j_2'+1)-j_1''(j_1''+1)-j_2''(j_2''+1)\}Q}. \quad (8)$$

Now $|H_{A1}'+H_{A2}'-H_{A1}''-H_{A2}''|\gg|j_1'(j_1'+1)+j_2'(j_2'+1)-j_1''(j_1''+1)-j_2''(j_2''+1)|Q$

except for the term where $i=4$, $H_{A1}'=H_{A1}''$, $H_{A2}'=H_{A2}''$, since the first vibrational, and *a fortiori* the first electronic frequency $\gg 2Q/h$. Therefore,

$$\varepsilon^{(2)}=\sum_{i=1}^{4}\sum_{H_{A1}''H_{A2}''}{}'\frac{|(H_{A1}'H_{A2}'|V_{i0}|H_{A1}''H_{A2}'')|^2}{H_{A1}'+H_{A2}'-H_{A1}''-H_{A2}''}\sum_{\beta'\beta''}\sum_{j_1''j_2''}\left\{\frac{|(j_1'j_2'\beta'|P_i|j_1''j_2''\beta'')|^2}{D}\right.$$

$$\left.-\frac{\{j_1'(j_1'+1)+j_2'(j_2'+1)-j_1''(j_1''+1)-j_2''(j_2''+1)\}Q}{H_{A1}'+H_{A2}'-H_{A1}''-H_{A2}''}\cdot\frac{|(j_1'j_2'\beta'|P_i|j_1''j_2''\beta'')|^2}{D}\right\}$$

$$+\frac{|(H_{A1}'H_{A2}'|V_{40}|H_{A1}'H_{A2}')|^2}{D}\sum_{\beta'\beta''}\sum_{j_1''j_2''}{}'\frac{|(j_1'j_2'\beta'|P_4|j_1''j_2''\beta'')|^2}{\{j_1'(j_1'+1)+j_2'(j_2'+1)-j_1''(j_1''+1)-j_2''(j_2''+1)\}Q}$$

$$+\text{terms of the order of }\frac{Q^2}{(H_{A1}'+H_{A2}'-H_{A1}''-H_{A2}'')^2}. \quad (9)$$

$\varepsilon^{(2)}$ is to be evaluated for parahydrogen[5] ($j_1'=j_2'=0$; $D=1$) and for orthohydrogen ($j_1'=j_2'=1$; $D=9$). The first term in curly brackets, summed over β'', j_1'' and j_2'' is

$$\frac{1}{D}\sum_{\beta'}(j_1'j_2'\beta'|P_i^2|j_1'j_2'\beta')=(00|P_i^2|00)$$

for both ortho and para states. Similar but more complicated operations show that the sums over the second term in curly brackets are likewise the same for ortho and para molecules. The last term of (9), substituting

$$\frac{9}{16}\frac{\tau^4}{r^{10}} \text{ for } |(H_{A1}'H_{A2}'|V_{40}|H_{A1}'H_{A2}')|^2$$

is, by direct computation,

$$-0.23333\frac{\tau^4}{Qr^{10}} \text{ for } p\text{-}H_2,$$

and

$$-0.18096\frac{\tau^4}{Qr^{10}} \text{ for } o\text{-}H_2.$$

Thus p-H_2 possesses, relative to o-H_2, an additional attractive term of the magnitude

$$-0.0524\frac{\tau^4}{Qr^{10}}=0.143\frac{\text{cal.}}{\text{mole}} \text{ for } H_2;$$

$$=0.286\frac{\text{cal.}}{\text{mole}} \text{ for } D_2.$$

This contribution is of the wrong sign, order of magnitude, and mass-dependence. (See § 5 Eq. (21).) The interaction of slowly-rotating quadrupoles[10] is thus not responsible for the vapor pressure differences. The general conclusion of this section is that if there is any appreciable difference in van der Waals energies between orthohydrogen pairs and parahydrogen pairs, it must be attributed to interaction between the rotational energy and the electronic or vibrational energy.

3. Effect of Rotational-Vibrational and Rotational-Electronic Interaction

We will therefore discard the assumption that electronic and vibrational levels are independent of rotational energy, and begin anew our calculations from Eq. (5). The picture now becomes highly complicated; for the excited states, the rotational selection rules are not the same as for the ground state, the rotational energy depends on the electronic and vibrational energy, and no simple generalization of the scheme exemplified by Eqs. (7), (8) and (9) can be made. We will therefore be compelled to use approximate methods. Eq. (5) may be transformed to

$$\varepsilon^{(2)}=\frac{1}{D}\sum_{\beta'}\frac{(H_0'\beta'|V^2|H_0'\beta')}{H_0'}$$
$$-\frac{1}{D}\sum_{\beta'\beta''}\frac{(H_0'\beta'|V|H_0'\beta'')(H_0'\beta''|V|H_0'\beta')}{H_0'}$$
$$+\frac{1}{D}\sum_{\beta'}\sum_{H_0''\beta''}{}'\frac{H_0''}{H_0'}$$
$$\times\frac{(H_0'\beta'|V|H_0''\beta'')(H_0''\beta''|V|H_0'\beta')}{H_0'-H_0''}. \quad (10)$$

The second term of (10) is either zero or negligible. Then

$$\varepsilon^{(2)}=\frac{1}{H_0'}\left\{\frac{2}{3}\frac{(\mu_1^2)_{Av}(\mu_2^2)_{Av}}{r^6}+\frac{(\mu_1^2)_{Av}(\tau_2^2)_{Av}}{r^8}\right.$$
$$\left.+\frac{(\mu_2^2)_{Av}(\tau_1^2)_{Av}}{r^8}+\frac{14}{5}\frac{(\tau_1^2)_{Av}(\tau_2^2)_{Av}}{r^{10}}\right\}$$
$$+\frac{1}{D}\sum_{\beta'}\sum_{H_0''\beta''}{}'\frac{H_0''}{H_0'}$$
$$\times\frac{(H_0'\beta'|V|H_0''\beta'')(H_0''\beta''|V|H_0'\beta')}{H_0'-H_0''}, \quad (11)$$

where the $(\mu_1^2)_{Av}$ indicates the average of μ_1^2 over the ground state of molecule one, etc. Following our experience with the H-atom calculations, we expect that for the usual choice of the energy zero (namely $H_0'=-2\times13.54$ ev) the second term will be considerably smaller than the first, and will be neglected henceforth.

Now

$$(\mu_1^2)_{Av}=(\mu_2^2)_{Av}=K_1c^2, \quad (\tau_1^2)_{Av}=(\tau_2^2)_{Av}=K_2c^4, \quad (12)$$

where c is the internuclear distance of the molecule in the ground state considered; K_1 and K_2 are integrals practically—we shall assume completely—independent of c.

We have, from (11) and (12)

$$\varepsilon^{(2)}\sim\frac{\alpha c^4}{r^6}+\frac{\beta c^6}{r^8}+\frac{\gamma c^8}{r^{10}}, \quad (13)$$

where α, β and γ are constants. Using Margenau's values[11] for the van der Waals constants, the contribution of $\varepsilon^{(2)}$ to the binding energy E_A of a cubic face-centered lattice is[8]

$$E_A=\frac{11.4\times10^{-60}}{r^6}\times\frac{N}{2}\times14.4539+\frac{31\times10^{-76}}{r^8}$$
$$\times\frac{N}{2}\times12.8019+\frac{45\times10^{-92}}{r^{10}}\times\frac{N}{2}\times12.3112 \quad (14)$$

or, in cal./mole, $596+114+13=723$. This value of the attractive energy is about correct to account for the high compressibility of H_2 and the depth of the energy minimum, 490 cal./mole.

Now, when the H_2 molecule takes on a quantum of rotational energy, it stretches an

[10] K. Clusius, Bunsengesellschaft **11**, 21 (1932).

[11] H. Margenau, J. Chem. Phys. **6**, 896 (1938).

amount given by[12]

$$\frac{\delta c}{c}=\frac{4B_0^2}{\omega_0^2}=7.60\times10^{-2}\ \%; \qquad (15)$$

for deuterium, $\frac{\delta c}{c}=3.80\times10^{-2}\ \%$.

From (13), (14) and (15)

$$\left.\begin{aligned}(E_A)_{o\text{-}H_2}-(E_A)_{p\text{-}H_2}&=596\times4\frac{\delta c}{c}\\&\quad+114\times6\frac{\delta c}{c}+13\times8\frac{\delta c}{c}=2.41\frac{\text{cal.}}{\text{mole}},\\(E_A)_{p\text{-}D_2}-(E_A)_{o\text{-}D_2}&=1.21\frac{\text{cal.}}{\text{mole}}.\end{aligned}\right\} \qquad (16)$$

We remark that $\Delta\varepsilon^{(2)}$ for a mixed pair (an ortho and a para molecule) will be intermediate between $\Delta\varepsilon_{\text{ortho}}{}^{(2)}$ and $\Delta\varepsilon_{\text{para}}{}^{(2)}$; thus, ortho and para molecules will form perfect solutions. Finally, it is emphasized that the values (16) for ΔE_A are based on a rather simplified view of rotational interaction, as reflected by the approximations employed, and should be considered as giving orders of magnitude only.

4. Generalities on Crystal Energies and Volumes

We undertake next the step from our calculated ΔE_A's to the observed quantities. The potential function for a pair of molecules is given essentially by

$$\phi=-E_A+E_R=-A/r^6+Be^{-r/\rho} \qquad (17)$$

with r determined by

$$\partial\phi/\partial r=0. \qquad (18)$$

We suppose ϕ to alter by a small change in A; B and ρ remaining constant. We have no reason to believe B and ρ *will* be constant: but we are considering only the van der Waals forces. From (18) we have $r=r(A)$, but

$$d\phi=\frac{d\phi}{dA}dA=\left\{\frac{\partial\phi}{\partial r}\frac{dr}{dA}+\frac{\partial\phi}{\partial A}\right\}dA=\left[\frac{\partial\phi}{\partial A}\right]_r dA.$$

Thus any change in r is without effect on the binding energies: and the change in ϕ_{minimum} is merely $-\Delta E_A$. The change in energy is, contrariwise, not without effect on the specific volume, which we may find from

$$\frac{dV}{V}=-\frac{3\theta}{6+\dfrac{\theta}{\theta-1}}\cdot\frac{d\phi_{\min}}{\phi_{\min}},\quad\text{where}\quad\theta=\frac{Be^{-r/\rho}}{A/r^6}. \qquad (19)$$

Taking

$$\theta=\frac{1}{3},\quad\frac{d\phi}{\phi}=\frac{2.4}{490},\quad V=25\ \text{cm}^3,$$

we find $dV=V_{o\text{-}H_2}-V_{p\text{-}H_2}=-0.022\ \text{cm}^3$: using the apparent experimental value of $d\phi_{\min}{}^{H_2}=-4.8$ (see next section), $dV=-0.044\ \text{cm}^3$.

Thus far we have been considering vibrationless solids. The dV of (19), for example, is the change in volume of a vibrationless solid; the change of volume is *measured* on a solid whose properties are much altered by an enormous energy of vibration. Similarly, the vapor pressure permits us to find the heat of sublimation $\chi=-\sum_{\text{lattice}}\phi_{\min}$ minus the zero-point vibrational energy, say E_0. E_0 depends on ϕ in some complicated and unknown fashion; the transition from $\phi_{\min}$ to χ, or vice versa, can only be made semi-empirically. We will therefore stop our theoretical development at $\Delta\phi_{\min}=-\Delta E_A$—the next step is properly the domain of a theory of molecular solids—and try to deduce as best we may an experimental value of $\Delta\phi_{\min}$.

5. Comparison with Experiment

Brickwedde, Scott and Taylor analyzed their data[4] and Keesom's[3] using the Clausius-Clapeyron equation, and found $\chi_p-\chi_o=1.8\pm1.5$ for solid D_2, 0.0 ± 1.5 for liquid D_2, -3.1 ± 0.7 for liquid H_2. A recalculation showed that these values depend on a necessarily arbitrary choice of $(d/dT)(\Delta p/p)$ and the calculated $\Delta\chi$'s seemed to have an exaggerated drift with the temperature. We therefore proceeded in a somewhat different fashion to avoid the large errors in the temperature coefficients. Subtracting (1) from (2), and defining both $\Delta\chi$ and Δp as positive

$$\Delta\chi=RT\frac{\Delta p}{p}-\left\{V_s+A\left(1+\frac{B}{T^2}\right)\right\}\Delta p. \qquad (20)$$

[12] Constants (usual spectroscopic notation) from C. R. Jeppesen, Phys. Rev. **45**, 480 (1934).

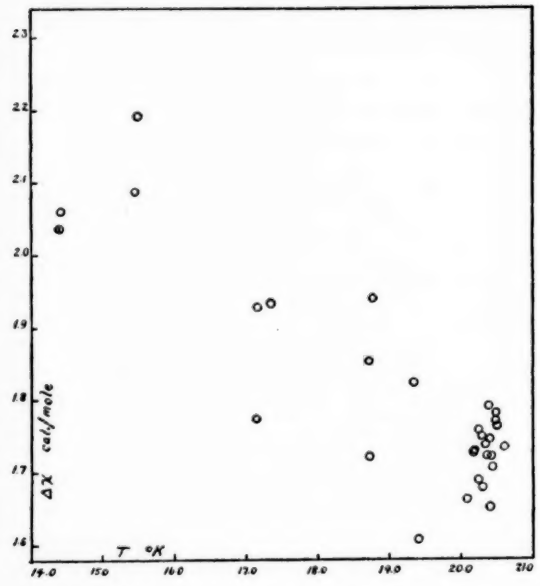

FIG. 1. $\chi_{o\text{-}H_2} - \chi_{p\text{-}H_2}$ measured at various temperatures.

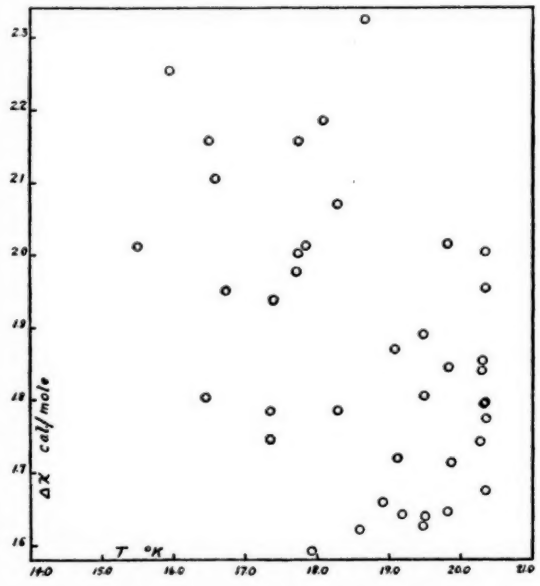

FIG 2. $\chi_{p\text{-}D_2} - \chi_{o\text{-}D_2}$ measured at various temperatures.

V_s is the molar volume, in liters, of the condensed state. $-RTA(1+B/T^2)$ is the second virial coefficient for the gas. For hydrogen we used the values $A=0.0311$ liters, $B=1527$; for deuterium, $A=0.0130$ and $B=5369$, to agree with the data of Schaefer.[13]

Figures 1 and 2 give the results of these calculations. The results for H_2 may be expressed as $\chi_{o\text{-}H_2} - \chi_{p\text{-}H_2} = \Delta\chi = \{1.743 - 0.072(T-20)\} \pm 0.05$. This is paradoxical, since $\Delta\chi$, the difference in ideal heats of vaporization at absolute zero, is a constant. The trend may be due to systematic error, or to the use at too low temperatures of an equation of state valid from $T=20°$ to $T=30°$. The results for D_2 do not fall quite so nicely. The mean value of all measurements of $\Delta\chi_{D_2} = \chi_{p\text{-}D_2} - \chi_{o\text{-}D_2}$ on the liquid state ($T=18.58°$ to $20.35°$) is $\Delta\chi_{D_2}^{19.45} = 1.78 \pm 0.1$ cal./mole; the corresponding value for H_2, either from the empirical equation or from a similar averaging is $\Delta\chi_{H_2}^{19.45} = 1.78 \pm 0.03$ cal./mole. These will be taken as the best values, since they are at a temperature where the equation of state is most probably valid, and near where most of the measurements were made.

Equation (20) has strictly been derived for solids only; yet the same form of equation will hold for liquids, with the ambiguity that $\Delta\chi$ is Δ (heat of vaporization) $+\Delta$ (heat of fusion). The data for D_2 (Fig. 2) seems to indicate no difference in behavior between the solid and the liquid states, and thus that Δ (heat of fusion) is much smaller than Δ (heat of vaporization). Whatever may be the objections to the foregoing method of calculation, the drift of the results is much smaller than the drift of the results reckoned from the Clausius-Clapeyron equation, and does not prevent us from determining with some assurance the sign and the magnitude of $\chi_{\text{ortho}} - \chi_{\text{para}}$.

The simplest way to pass from $\Delta\chi$ to $\Delta\phi_{\min}$ is to assume that $\Delta\phi_{\min} : \Delta\chi$ as $-490 : 183$ in the case of H_2, and as $-490 : 274$ in the case of D_2, following the gross ratios of $\phi_{\min}/\chi$.[14]

This gives

$$\left.\begin{aligned}(E_A)_{o\text{-}H_2} - (E_A)_{p\text{-}H_2} &= -\Delta\phi_{\min}{}^{H_2} = 4.76 \pm ?,\\ (E_A)_{p\text{-}D_2} - (E_A)_{o\text{-}D_2} &= -\Delta\phi_{\min}{}^{D_2} = 3.18 \pm ?.\end{aligned}\right\} \quad (21)$$

Naturally this somewhat naive calculation will only give approximate results,[15] which we indicate by the $\pm ?$.

On comparing (21) with (16) we see that the experimental values are somewhat higher. It is

[13] K. Schaefer, Zeits. f. physik. Chemie **B36**, 85 (1937).

[14] K. Clusius and E. Bartholomé, Zeits. f. physik. Chemie **B30**, 237 (1935).

[15] $\phi_{\min}$ itself is estimated on the assumption of simple harmonic forces, and it is difficult to say how correct it may be.

possible that this difference is outside the limit of approximations to (21) and (16), in which case it might be ascribable to the contribution of the exchange energies. It is to be remembered that the division of the intermolecular energy into an "exchange-repulsive" part and a "van der Waals-attractive" part is at its worst near the energy minimum. From this point of view the above calculations are an approximation to $\Delta\phi_{\min}$ "from the further side of the minimum." It is obvious that there will be another approximation "from the nearer side of the minimum," but there seems no point in opposing the two approximations as two different causes of the same phenomenon. In any event the theoretical quantities are of the correct order of magnitude, sign, and variation with mass.

The data on changes in volume are given by Scott and Brickwedde[16] who find $V_{o\text{-}H_2} - V_{p\text{-}H_2} = -0.185 \pm 0.013$ cm³/mole with $V = 28.397$ cm³/mole ($T = 20.38°$K). This value cannot be directly compared with those calculated from (19), not only because of the influence of vibrational energy, but also because the measured quantity is of a liquid state. The sense of the relation between dV (vibrationless) and dV (vibrating) cannot be intuitively discerned, and it appears most discreet, at present, to content ourselves with the correct sign and order of magnitude. We should not be surprised, following the remarks of the last paragraph, to note that a greater attractive force for o-H_2 will give us the same direction of shift of the position of $\phi_{\min}$ as a lesser repulsive force.[16, 17]

[16] R. B. Scott and F. G. Brickwedde, J. Chem. Phys. **5**, 736 (1937).

[17] During the preparation of this paper an article by K. Schaefer (Naturwiss. **26**, 563 (1938)) appeared, giving an alternative and contrary explanation of the phenomenon

6. Acknowledgment

The authors wish to thank Professor G. E. Uhlenbeck for criticism of the manuscript.

MARCH, 1939 JOURNAL OF CHEMICAL PHYSICS VOLUME 7

Spectroscopic Evidence of Hydrogen Bonds: Chloroform and Bromoform in Donor Solvents

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(Received December 2, 1938)

The method of infra-red spectroscopy has been used to study solutions of chloroform and bromoform in various electron donor solvents, including ketones, esters, ethers and amines. In the region of 4μ, a band has been observed which apparently is not characteristic of the spectrum of either the solute or solvent. Because of the intensity of the band it is thought to be a fundamental. The most reasonable interpretation seems to be that it is an NH or OH vibrational band resulting from intermolecular hydrogen bond formation between the CH haloform group and a N or O of the solvent. The band for the bromoform solutions is weaker than that for the corresponding chloroform solutions.

Introduction

An interesting case of association between dissimilar molecules is that of the haloforms with other liquids. The physical properties, such as vapor pressures, viscosities and dielectric constants of mixtures of chloroform with donor[1] liquids like acetone or ether are abnormal.[2] Also the solubilities of haloforms in donor solvents are known to be abnormal.[3] Chloroform has been found to cause pronounced variations in the spectrum of ether and similar solvents.[4]

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[1] The term "donor" is used throughout this paper to mean donor of an electron pair.

[2] D. B. Macleod and F. J. Wilson, Trans. Faraday Soc. **31**, 596 (1935); S. Glasstone, *ibid.* **23**, 200 (1936); R. H. Ewell, J. Chem. Phys. **5**, 967 (1937).

[3] G. F. Zellhoefer, M. T. Copley and C. S. Marvel, J. Am. Chem. Soc. **60**, 1337 (1938).

[4] W. Gordy, J. Am. Chem. Soc. **60**, 605 (1938).

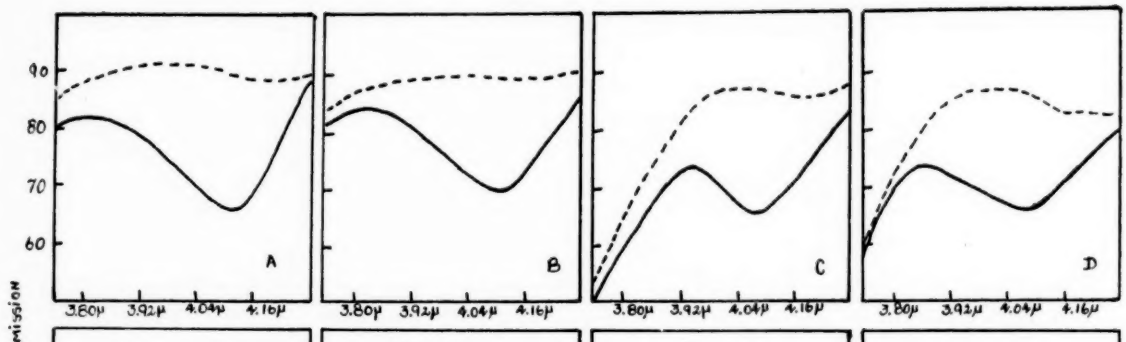

FIG. 1. Experimental (solid line) and theoretical (broken line) transmission of some chloroform solutions. Mole fraction 0.5. Cell thickness 0.015 cm. Solvent (A) acetone; (B) methyl ethyl ketone; (C) di-ethyl ether; (D) dioxan; (E) amyl acetate; (F) pyridine; (G) *a*-picoline; (H) piperidine.

Many investigators suggest that these effects may be due to hydrogen bonding between the CH haloform group and a suitable atom of the solvent. Association of this type should cause variations in the vibrational band of the CH haloform group, but the changes in most cases would be difficult to measure because of the overlapping CH absorption of the solvent. Recently the expected variations in the CH band have been detected for chloroform-quinoline mixtures.[5]

The formation of hydrogen bonds through a CH group does not occur generally.[6] It is quite possible, however, that the presence of the electronegative halogens attached to the haloform carbon would decrease its attraction for the proton sufficiently to allow hydrogen bonding to occur with a suitable atom. Because of the wide interest in this problem the author has continued his spectroscopic studies of chloroform mixtures and has made some measurements on bromoform mixtures.

RESULTS

For several of the mixtures there was observed in the region of 4μ a band which seems not to be characteristic of either component of the mixture. Fig. 1 shows the observed transmission of eight chloroform mixtures in the region 3.74μ to 4.28μ. In the same figure are shown theoretical curves of these mixtures as calculated from Beer's law. The differences in the theoretical and observed transmissions are striking and give proof that some type of interaction occurs. Data were also obtained for mixtures of chloroform with *n*-butyl ether and with isopropyl ether; the curves are similar to that given for di-ethyl ether-chloroform mixture.

In Fig. 2 are given transmission curves for three bromoform mixtures. Here, too, the differences between the theoretical and observed transmissions are pronounced but not as great as for the corresponding chloroform mixtures.

[5] A. M. Buswell, W. H. Rodebush and M. F. Roy, J. Am. Chem. Soc. **60**, 2528 (1938).
[6] M. L. Huggins, J. Org. Chem. **1**, 452 (1936).

A curve obtained for an acetone-bromoform mixture showed no appreciable variation from the curve calculated from Beer's law.

Figure 3 shows the transmission of pure chloroform and of pure bromoform in the region 3.20μ to 4.53μ.

Discussion

If the cause of this absorption in the haloform mixtures can be ascertained it should be of great help in determining the nature of the complex formations. For some of the mixtures certainly the intensity of the band is rather great for it to be regarded as a harmonic of a fundamental occurring at longer wave-lengths.[7] The associational band in the *a*-picoline-chloroform mixture, Fig. 1G, for example, is almost as strong as the CH fundamental of the pure chloroform, Fig. 3. While the cell thickness for the pure chloroform is only one-half that of the mixture, the concentration of the mixture is such that there are approximately the same number of chloroform molecules involved in both cases. There is a small band appearing in the spectrum of pure chloroform at 4.15μ and a similar band for bromoform at 4.38μ. The fact that these small bands occur near the associational band seems to be purely coincidental. If it were possible for them to be intensified and shifted thus by the solvent, there would remain the question why the bromoform band is shifted more than that of the chloroform. The rather strong associational band in liquid water at 4.7μ is thought to be a combination band[8] of the 6μ fundamental and a frequency of hindered rotation occurring in the far infra-red. A similar interpretation does not seem possible here. If the band is a fundamental, it must arise from a vibration involving hydrogen. One would hardly interpret it as due to changes in the vibrational energy between two heavy atoms like N or O: the force constant required would be too great for a frequency as high as this. One might suppose it to be the CH band of the chloroform or bromoform which had been shifted to the longer wave-lengths because of hydrogen bond formation. Nevertheless, the magnitude of the shift required would be much greater than that of any found for the OH band of alcohols, phenols, etc., which form rather strong hydrogen bonds. Also, for the stronger proton-attracting solvents, like pyridine, the band occurs at shorter wave-lengths than for

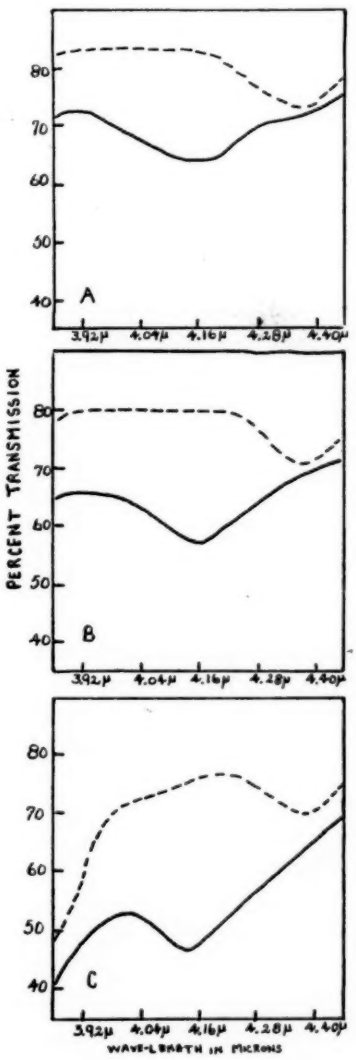

FIG. 2. Experimental (solid line) and theoretical (broken line) transmission of some bromoform solutions. Mole fraction 0.5. Cell thickness 0.015 cm. Solvent (A) pyridine; (B) *a*-picoline; (C) piperidine.

[7] After the data given here had been obtained and a brief announcement had been sent to Nature (**142**, 831 (1938)), the paper by Buswell, Rodebush and Roy (reference 5) appeared, showing that they have observed this band in mixtures of chloroform with acetone, ethyl ether and quinoline. They were of the opinion that the band could be a second harmonic of a $CHCl_3$ band, which had been greatly altered by the solvent.

[8] J. W. Ellis, Phys. Rev. **38**, 693 (1931); P. C. Cross, J. Burnham and P. A. Leighton, J. Am. Chem. Soc. **59**, 1134 (1937).

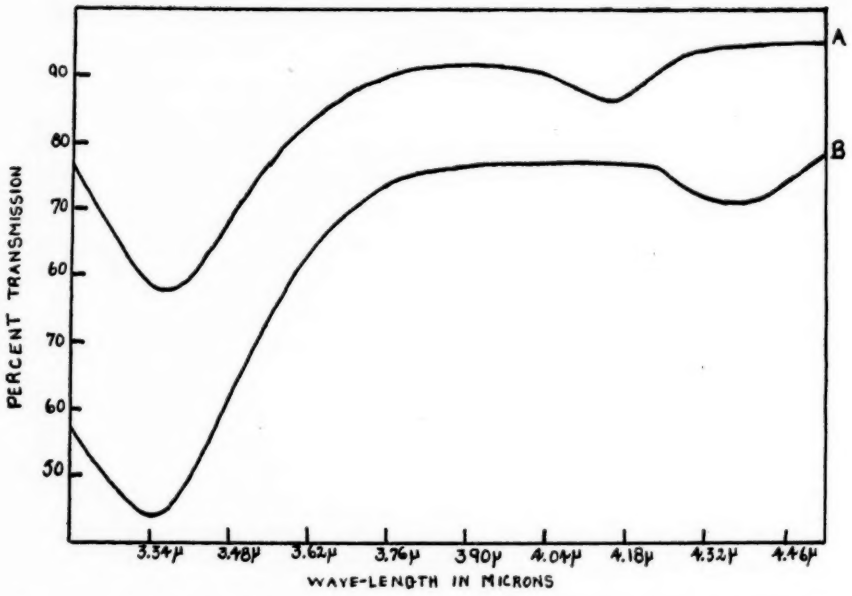

FIG. 3. Transmission of pure chloroform (curve A) and pure bromoform (curve B). Cell thickness 0.0075 cm.

weaker proton-attracting solvents, like acetone or ether. If this were the shifted CH band, the opposite would be expected. The interpretation which seems most reasonable to the author is that this is an NH or OH vibrational band resulting from the new bond formed by the sharing of the proton of the CH group with the N or O of the solvent. In most cases of hydrogen bonding perhaps only one minimum exists in the potential energy curve of the hydrogen, and it would be more correct to think of the proton as oscillating between the two bridged atoms rather than vibrating against either. It is not impossible, however, that the effective charges on the two atoms held by the proton, and the distance between them, may be such that double minima exist in the potential energy function of the proton, which could give rise to two separate vibrational bands. In consideration of the fact that for most of the mixtures the association probably does not involve more than 30 or 40 percent of the molecules—from their studies of the heat of mixing, Macleod and Wilson[2] estimated that in an equimolecular mixture of ether and chloroform only 15 to 20 percent of the molecules are combined at 15°C—the intensity of the associational band is such as to permit its being regarded a fundamental. The above interpretation is in agreement with the fact that the band appears at longer wavelengths for the weaker donor solvents, and that, for a given solvent, it appears at longer wavelengths and is less intense for a bromoform than for a chloroform mixture. The force constants of the OH and NH bond calculated from the frequencies of the associational bands, on the assumption of simple harmonic force functions, are approximately one-half those of the ordinary OH and NH bonds.

The author is indebted to Dr. H. H. Nielsen and to Dr. Alpheus W. Smith, who made this work possible.

Spectroscopic Evidence of Hydrogen Bonds: Aniline and Some Substituted Phenols

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(Received December 2, 1938)

Both inter- and intra-molecular hydrogen bonding in certain substituted phenols was studied by determining the effect of the bonding on the OH fundamental occurring in the region of 3μ. For *m*- and *o*-nitro-phenols, complex formation with certain oxygenated solvents was studied. The vibrational band of the NH_2 aniline group was found to shift to wave-lengths shorter by 0.07μ upon dilution of aniline in benzene solution. Association of the aniline in the liquid state through very weak hydrogen bonds is proposed as an explanation of this shift. Similar evidence is offered for the formation of very weak hydrogen bonds between aniline and the solvents *n*-butyl and isopropyl ethers.

INTRODUCTION

INFRA-RED spectroscopy has been used to considerable advantage in the study of the hydrogen bond theory. The usual method of approach is to determine the effects of the hydrogen bonding on the absorption of the group which carries the hydrogen. In a few instances it has been found possible to measure the effects on certain other groups. For example, the linking of methyl alcohol through its OH group to the C=O group of acetone has been found to shift the C=O band to lower frequencies and to intensify it appreciably.[1] The effects of the bonding on the OH fundamental are similar but more pronounced than those on the C=O band. The second harmonic of the OH band is either very diffuse and weak or absent entirely when the OH is involved in a strong bond.[2] The absence of absorption in the region of the OH harmonic has often been taken as an empirical criterion for the presence of strong hydrogen bonds.

In the present investigation a study has been made of the OH fundamental of several substituted phenols for which the OH harmonic is absent. Also, measurements on aniline were included as there is some question whether the NH_2 aniline group shares its protons in hydrogen bond formation. The data were obtained with a Wadsworth-Littrow type prism instrument described in detail by Strong.[3]

DISCUSSION OF RESULTS

Substituted phenols

Certain ortho substituted phenols are among those compounds thought to be chelated because they do not absorb in the region of the OH harmonic. Some of these—*o*-nitro-phenol, salicylaldehyde, methyl salicylate, and phenyl salicylate—were chosen for study in the region of the fundamental.[4]

Figure 1 shows some results which were obtained for *o*-nitro-phenol in benzene solutions. The departure of the solution curve in the region of 3μ from the curve for pure benzene demonstrates that there is absorption which may be attributed to the OH group.

Figure 2 makes possible a comparison of the absorption of *o*-, *p*- and *m*-nitro-phenols in benzene solution. The curves given represent the ratio of the transmission of the solution to that of an equal thickness of pure solvent. The curve for *p*-nitro-phenol has only one minimum, and this occurs at 2.77μ. This is about the position of the monomolecular OH band of phenol in dilute solution in inert solvents.[5, 6] In the curves

* Present address: Mary Hardin-Baylor College, Belton, Texas.

[1] W. Gordy, Phys. Rev. **50**, 1151 (1936); J. Am. Chem. Soc. **60**, 605 (1938).

[2] G. E. Hilbert, O. R. Wulf, S. B. Hendricks and U. Liddel, Nature **135**, 147 (1935); J. Am. Chem. Soc. **58**, 548 (1936); **58**, 1991 (1936).

[3] J. Strong, Rev. Sci. Inst. **2**, 585 (1931).

[4] (a) Although they did not publish their curves, A. M. Buswell, V. Dietz and W. H. Rodebush (J. Chem. Phys. **5**, 501 (1937)) have reported absorption in some of the ortho substituted phenols which they ascribe to the OH fundamental. (b) J. Errera and H. Sack (Trans. Faraday Soc. **34**, 728 (1938)) have published data showing that salicylaldehyde absorbs in the region of 3μ.

[5] J. J. Fox and A. E. Martin, Proc. Roy. Soc. (London), **A162**, 419 (1937).

[6] W. Gordy and A. H. Nielsen, J. Chem. Phys. **6**, 12 (1938).

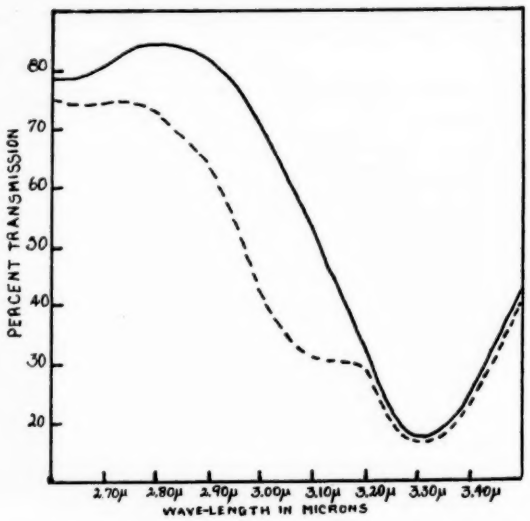

FIG. 1. Pure benzene (solid line) 0.032 cm; 0.3 *M* *o*-nitro-phenol solution in benzene (broken line) 0.032 cm.

for *m*-nitro-phenol, which are for slightly more concentrated solutions, two minima occur. The longer wave-length component is no doubt caused by intermolecular association, as chelation would not be possible here because of steric hindrance. Its position is near that of ordinary phenol in the associated state.[5, 6] For the *o*-nitro-phenol there is no evidence of a minimum at 2.77μ. There is, however, a definite band, the center of which appears at 3.03μ. There is a corresponding band in salicylaldehyde, methyl salicylate and phenyl salicylate, as may be seen from Fig. 3. The fact that the minima for these orthophenols are found at about 3μ rather than at about 2.77μ is strong evidence for chelation through hydrogen bonds. This result was suggested by the earlier work on the harmonic.[2] These measurements on the fundamental make possible a comparison of the strengths of the various hydrogen bonds by the magnitude of the shifts they produce in the OH fundamental. A comparison of shifts is of course impossible in the case of measurements on the harmonic where the absence of absorption is taken as the evidence for the presence of the bond. It has not yet been theoretically demonstrated why the OH harmonic does not appear. The answer may lie in the fact that the hydrogen bonding has increased the symmetry and made the force function more nearly a Hooke's-law function. This possibility has been suggested before.[4b]

The appearance of the OH fundamental of ordinary phenol at longer wave-lengths and its greater intensity for solutions of phenol in active solvents like ether than for dilute solutions in inert solvents like benzene are thought to be consequences of complex formation.[6] It is instructive to compare the OH absorption of the *o*- and *m*-forms of a substituted phenol in active solvents.

In Fig. 4 are shown transmission curves for *o*- and *m*-nitro-phenols in three oxygenated solvents. The curve for *m*-nitro-phenol in benzene solution is repeated to facilitate comparison. For *m*-nitro-phenol in nitro-benzene the band is broad and intense, with its center at about 2.85μ. The differences between this curve and that for the same concentration of *m*-nitro-phenol in benzene solution are, in the author's opinion, sufficient proof of complex formation through

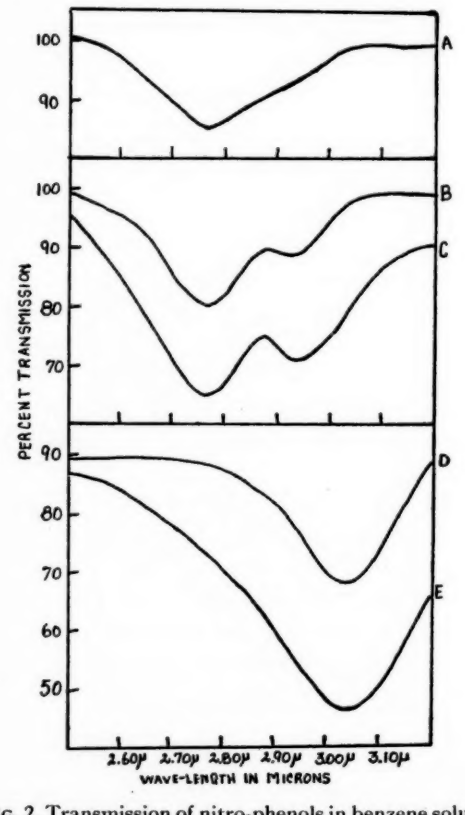

FIG. 2. Transmission of nitro-phenols in benzene solution. Cell thickness 0.032 cm. (A) 0.065 *M* *p*-nitro-phenol; (B) 0.075 *M* *m*-nitro-phenol; (C) 0.15 *M* *m*-nitro-phenol; (D) 0.15 *M* *o*-nitro-phenol; (E) 0.5 *M* *o*-nitro-phenol.

intermolecular hydrogen bonds. Yet the attraction of the *o*-nitro-benzene oxygens for the protons is not sufficient to break the chelation bonds of nitro-phenol. This is evidenced by the similarity of the curve for *o*-nitro-phenol in nitro-benzene to that for *o*-nitro-phenol in benzene. The hydrogen bonds between the *m*-nitro-phenol and the solvent as measured by the shift in the OH band are stronger for the solvent ethyl acetate than for nitro-benzene, and stronger for *n*-butyl ether than for ethyl acetate. This agrees with the comparison of the proton-attracting properties of these solvents recently made by the author from their relative effects on the hydroxyl band of heavy alcohol.[7] The

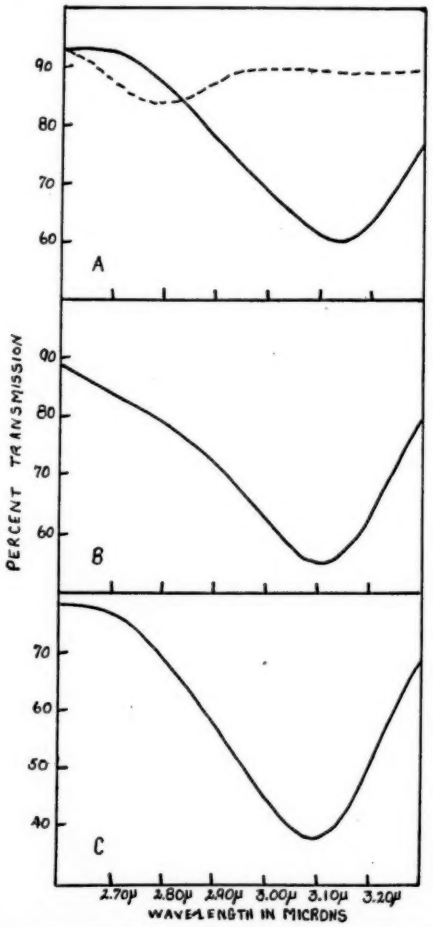

FIG. 3. Transmission of some substituted phenols in benzene solution. Cell thickness 0.032 cm. (A) 0.3 *M* *o*-hydroxy-benzaldehyde (solid line), 0.045 *M* *p*-hydroxy-benzaldehyde (broken line); (B) 0.3 *M* methyl salicylate; (C) 0.5 *M* phenyl salicylate.

[7] W. Gordy, J. Chem. Phys. 7, 93 (1939).

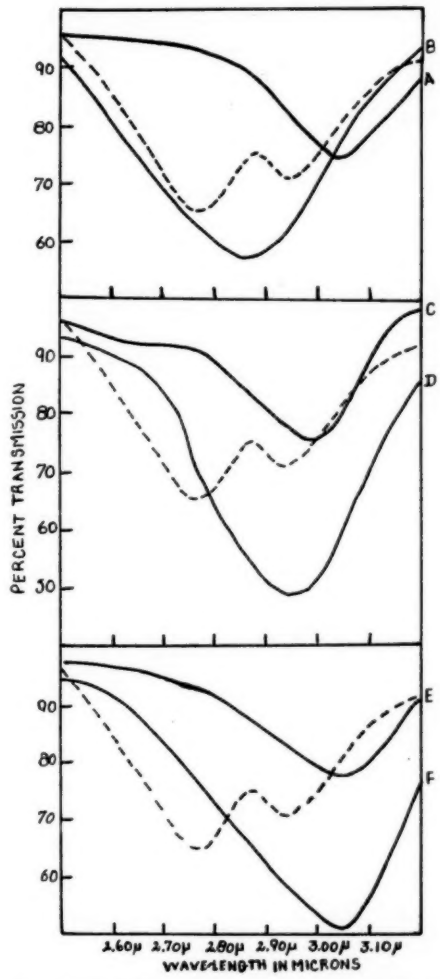

FIG. 4. Transmission of nitro-phenols in solution. Cell thickness 0.032 cm. Concentration 0.15 *M* Solid lines: (A) *o*-nitro-phenol in nitro-benzene; (B) *m*-nitro-phenol in nitro-benzene; (C) *o*-nitro-phenol in ethyl acetate; (D) *m*-nitro-phenol in ethyl acetate; (E) *o*-nitro-phenol in *n*-butyl ether; (F) *m*-nitro-phenol in *n*-butyl ether. Broken line: *m*-nitro-phenol in benzene.

o-nitro-phenol band in ethyl acetate solution is apparently shifted to wave-lengths slightly shorter than those of the band for the *o*-nitro-phenol in benzene solution. This shift may mean that the ethyl acetate is associated to some degree with the *o*-nitro-phenol. The small variation in the band, however, would lead one to conclude that the tendency of the ethyl acetate to break the chelation bonds is very slight. The *o*- and *m*-nitro-phenol bands for the *n*-butyl ether solution and the *o*-nitro-phenol band for the benzene solution all appear at approximately the same position. The very great difference in

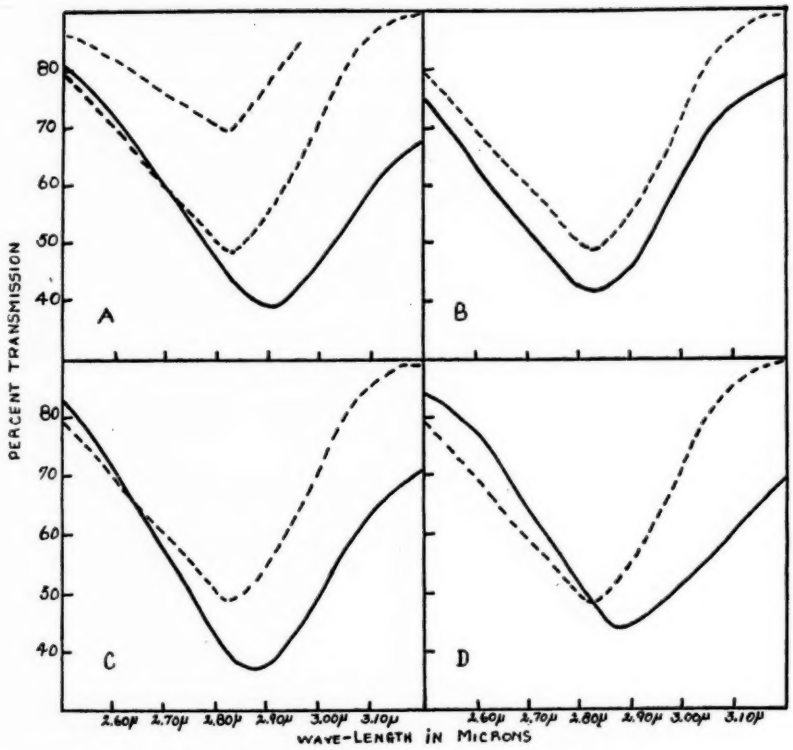

FIG. 5. (A) Solid line: pure aniline, $t=0.001$ cm; broken lines: aniline in benzene, $t=0.032$ cm (top curve, 0.5 M; bottom curve 1 M). (B) Solid line: 1 M aniline in nitro-benzene, $t=0.032$ cm; broken line: 1 M aniline in benzene, $t=0.032$ cm. (C) Solid line: 1 M aniline in n-butyl ether, $t=0.032$ cm; broken line: 1 M aniline in benzene, $t=0.032$ cm. (D) Solid line: 1 M aniline in isopropyl ether, $t=0.032$ cm; broken line: 1 M aniline in benzene, $t=0.032$ cm. The solution curve in every case represents the ratio of the transmission of the solution to that of an equal thickness of the pure solvent.

the intensities of the two bands for the n-butyl ether solutions favors the interpretation that the ortho substituted phenol remains largely chelated and hence does not associate appreciably with the solvent. The results presented here are in excellent accord with data[8] obtained from heats of mixing, solubilities, etc.

Aniline

In general the tendency of the amines to associate is known to be less than that of hydroxyl compounds.[9] Because there is evidence that the amine nitrogen has strong electron donor properties,[10] this low tendency for association in the primary and secondary amines is probably due to the weak acceptor properties of their hydrogens. Zellhoefer, Copley and Marvel[11] have suggested intermolecular association in aniline through N−H−N bonds as a possible explanation of the low solubility of certain haloforms in this liquid. Some time ago the author measured the absorption of the NH_2 aniline group for mixtures of aniline with CCl_4 and with certain oxygenated solvents.[12] Some evidence was found for complex formation between the aniline and the active solvents. Unfortunately measurements were made only for 1 : 1 mixtures. As there is still some uncertainty whether aniline in the liquid state is associated through hydrogen bonds, it was

[8] E. N. Lassettre, Chem. Rev. **20**, 259 (1937).
[9] M. L. Huggins, J. Org. Chem. **1**, 407 (1936).
[10] The author has found that certain amines produce pronounced variations in the hydroxyl band of alcohol. See reference 7.
[11] G. F. Zellhoefer, M. J. Copley and C. S. Marvel, J. Am. Chem. Soc. **60**, 1337 (1938).
[12] W. Gordy, J. Am. Chem. Soc. **59**, 464 (1937).

decided to supplement the previous information with measurements upon more dilute solutions than those previously studied.

Figure 5A shows a comparison of the NH_2 absorption of pure liquid aniline with concentrations of 1 M and 0.5 M aniline in benzene solution. The minimum in the solution curve appears at 2.83μ, while that of the pure liquid appears at 2.90μ. This difference in position probably indicates that weak hydrogen bonds are formed between the molecules in the liquid state. In the previous work[12] no shift was observed for the solution of CCl_4; this is doubtless attributable to the high concentration used. It is interesting to note that this shift of 0.07μ is about one-third that of the OH band in methyl alcohol upon dilution in an inert solvent.[5] The similarity of the NH_2 band in nitro-benzene to that in benzene, Fig. 5B, is good evidence that aniline does not form complexes with the nitro-benzene. The results indicate some interaction, though, when the solvent is *n*-butyl or isopropyl ether, Fig. 5C and D. Although the shift from the liquid state is to the shorter wave-lengths, the band appears at longer wave-lengths for solutions in each of these solvents than it does for the benzene solution.

The author is grateful to Dr. H. H. Nielsen and to Dr. Alpheus W. Smith, who made this work possible.

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The Thermodynamic Functions of Cyanogen and the Cyanogen Halides

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(Received December 24, 1938)

The free energy function, heat content and heat capacity of cyanogen and the cyanogen halides, ClCN, BrCN and ICN, have been calculated for a series of temperatures from spectroscopic and electron diffraction data. Since no experimental value for the carbon-iodine distance has been as yet obtained, an extrapolation is made from the values for the carbon-chlorine and carbon-bromine distances in the corresponding cyanogen compounds. 1.96 ± 0.04A is obtained for the I−C distance in cyanogen iodide. The free energies of formation of gaseous $(CN)_2$, ClCN and ICN have been calculated from thermal and equilibrium data. The values of $\Delta F^\circ_{298.1}$ are, 69.1 kcal./mole for $(CN)_2$, 35.5 kcal./mole for ClCN, and 46.75 kcal./mole for ICN. It is estimated that for gaseous BrCN $\Delta F^\circ_{298.1}=40$ kcal./mole.

SUFFICIENT spectroscopic and electron diffraction data have recently become available to permit the calculation of the free energy function $(-((F^\circ-E_0^\circ)/T))$, the entropy, the heat content and the heat capacity of the interesting set of linear molecules, cyanogen and the cyanogen halides, in the gaseous state. The fact that the data only suffice to make the calculations to the rigid-rotator, harmonic oscillator approximation should not decrease the usefulness of a tabulation of the above-mentioned functions. By combination with recently acquired thermal data it is furthermore possible to calculate more reliable values of the free energy of formation of cyanogen, cyanogen chloride and cyanogen iodide than have appeared heretofore.

The methods of calculation have been amply described in the literature.[1] In accordance with the convention adopted by writers in this field the *International Critical Tables*' values of the fundamental physical constants have been used.[2]

For cyanogen chloride, bromide and iodide the frequency assignment of West and Farnsworth[3] has been accepted (see Table I). No correction of their frequencies has been made although

* National Research Fellow in Chemistry.

[1] (a) L. S. Kassel, Chem. Rev. **18**, 277 (1936); (b) W. F. Giauque, J. Am. Chem. Soc. **52**, 4808 (1930); (c) A. R. Gordon and C. Barnes, J. Chem. Phys. **1**, 297 (1933).

[2] $R=1.9869$ cal./mole. $hc/k=1.4324$ cm degrees.

[3] W. West and M. Farnsworth, J. Chem. Phys. **1**, 402 (1933).

TABLE I. *The frequency assignment used.*

	ClCN	BrCN	ICN	NC−CN
ν_1	729 cm^{-1}	580	470	860
ν_2	2201	2187	2158	2150
ν_3	—	—	—	2336
$2\delta_1$	397	368	221	230
$2\delta_2$	—	—	—	512

their values were obtained from the Raman spectra of the liquids and methyl alcohol solutions of the compounds. The error introduced by the resultant uncertainty of the frequencies is undoubtedly completely negligible. Woo and Badger[4] and Woo, Liu and Chu[5] have discussed the assignments of the fundamental frequencies of cyanogen. Their assignments differ only in the value of the symmetric stretching frequency associated with the carbon-carbon bond, designated in Table I as ν_1. The value chosen by Badger and Woo,[4] 860 cm^{-1}, gives much better agreement with the electron diffraction value for the carbon-carbon distance than the assignment of Woo, Liu and Chu, 756 cm^{-1}, when Badger's rule is used to estimate the distance from the frequency. 860 cm^{-1} gives 1.35A, 756 cm^{-1} gives 1.41A while the new electron diffraction value is 1.36A. Hence 860 cm^{-1} has been used for ν_1.

Pauling, Springall and Palmer[6] have recently redetermined the interatomic distances in cyanogen. Their values of 1.36A for the carbon-carbon distance and 1.16A for the nitrogen-carbon distance have been used to calculate the moment of inertia rather than the earlier values by Brockway[7] since the newer photographs are much more satisfactory than the earlier ones.

Beach and Turkevich[8] have found 1.67A and 1.79A for the carbon-chlorine and carbon-bromine distances in cyanogen chloride and cyanogen bromide, and 1.13A for the carbon-nitrogen distance in both molecules, by the electron diffraction method. There are several independent methods by means of which one can extrapolate carbon-chlorine and carbon-bromine distances to obtain the carbon-iodine distance in cyanogen iodide.

TABLE II. *The interatomic distances and moments of inertia.*

	ClCN	BrCN	ICN	NC−CN
$x-C$	1.67A	1.79	1.96	1.36
$C\equiv N$	1.13	1.13	1.13	1.16
Moment of Inertia	142×10^{-40} gcm^2	200×10^{-40}	249×10^{-40}	175×10^{-40}
Symmetry No.	1	1	1	2

From the West and Farnsworth[3] frequencies for the cyanogen halides one can calculate values for the force constants of the carbon-halogen bonds in the three halides if one assumes the simple potential function:[9]

$$V=\tfrac{1}{2}k_1\Delta^2_{12}+\tfrac{1}{2}k_2\Delta^2_{23}. \qquad (1)$$

Badger's rule[10a] relates the interatomic distance to the force constant of the bond and the rows in the periodic system of the atoms forming the bond, (Relation I).[10b]

$$r_e=\left(\frac{C_{ij}}{k_e}\right)^{\frac{1}{3}}+d_{ij}. \qquad (2)$$

Taking Badger's values[10b] of $C_{ij}^{\frac{1}{3}}$ and d_{ij} and the force constants for the bonds calculated from the relation

$$k=4\pi^2\mu\nu^2c^2 \qquad (3)$$

one finds for Cl−CN, Cl−C = 1.63A; for BrCN, Br−C = 1.75A and for ICN, I−C = 1.93A. Since the C−Cl and C−Br so calculated are each 0.04A shorter than the experimental values one can assume an empirical correction of 0.04A and thus I−C = 1.97A.

A second relation of the same form as (2) has been proposed,[10c] differing from (2) in that C_{ij} and d_{ij} are determined by the groups in the periodic system to which the atoms "i" and "j" belong. One can use the force constants and distances found for the chloride and bromide to evaluate C_{ij} and d_{ij} and then calculate I−C from the cyanogen iodide force constant. This method yields 2.01A for the iodine-carbon distance.

Since the carbon-chlorine and carbon-bromine distances in the cyanogen compounds are 0.09A

[4] S. C. Woo and R. M. Badger, Phys. Rev. **39**, 432 (1932).
[5] S. C. Woo, T. Liu and T. C. Chu, J. Chinese Chem. Soc. **3**, 301 (1935); S. C. Woo, J. Phys. Chem. **B37**, 399 (1937).
[6] L. Pauling, H. D. Springall and K. J. Palmer, private communication.
[7] L. O. Brockway, Proc. Nat. Acad. Sci. **14**, 868 (1933).
[8] J. Y. Beach and A. Turkevich, J. Am. Chem. Soc., in publication.
[9] See for instance J. W. Linnett and H. W. Thompson, J. Chem. Soc. 1399 (1937).
[10a] R. M. Badger, J. Chem. Phys. **2**, 128 (1934).
[10b] R. M. Badger, J. Chem. Phys. **3**, 710 (1935).
[10c] R. M. Badger, Phys. Rev. **48**, 284 (1935).

and 0.12A shorter than the covalent distances (1.76 and 1.91A, respectively), a linear extrapolation yields 0.15A for the expected shortening in cyanogen iodide. The covalent bond distance for the carbon-iodine bond is 2.09A. This extrapolation thus gives 1.94A for the carbon-iodine distance in ICN.

If one assumes that the relationship between double bond character and bond shortening found by Pauling and Brockway[11] to obtain for carbon-carbon bonds is applicable to carbon-halogen bonds one finds that the observed distances for cyanogen-chloride and cyanogen-bromide correspond to 16.5 percent and 22.5 percent double bond character, respectively. A linear extrapolation gives 28.5 percent double bond character for the I−C bond in ICN or 1.94A. The average of the four estimates is 1.96A.

Table I summarizes the frequencies used in the calculating of the various thermodynamic functions while Table II contains the interatomic distances and the moments of inertia calculated from them. Average atomic weights have been used in calculating the moments of inertia since the error introduced by this approximation has been shown to be negligibly small.[12]

$-((F°-E_0°)/T)$, $(H°-E_0°)$ and $S_{298.1}$ are given in Table III, and C_p is given in Table IV. These quantities are for the ideal gases at a pressure of one atmosphere. The contributions of nuclear spin have been omitted.

[11] L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **59**, 1223 (1937).

[12] D. P. Stevenson and J. Y. Beach, J. Chem. Phys. **6**, 25 (1938).

TABLE IV. *The heat capacities of the ideal gases.* C_p *cal./mole degree.*

T°K	ClCN	BrCN	ICN	NCCN
250	10.13	10.59	11.10	12.79
300	10.72	11.14	11.57	13.60
350	11.17	11.55	11.90	14.25
400	11.53	11.85	12.15	14.78
450	11.82	12.10	12.35	15.22
500	12.07	12.32	12.54	15.62

THE FREE ENERGY OF FORMATION OF ClCN, ICN AND (CN)

Bichowsky and Rossini[13] give −36.5 kcal./mole for the heat of formation of gaseous ClCN at 18°C. $(H°-E_0°)_{291.1}=0.234$ kcal./mole for graphite,[14] 2.02 kcal./mole for N_2, 2.13 kcal./mole for Cl_2 and 2.46 kcal./mole for ClCN. For the reaction $C_{\beta g}=C_{\text{diamond}}$, $\Delta H_{291.1}=0.22$ kcal./mole.[13] Thus

$$C_{\beta g}+\tfrac{1}{2}N_2+\tfrac{1}{2}Cl_2=(ClCN)_{(g)},\qquad \Delta E_0°=36.5 \text{ kcal./mole.}$$

From Table III and the work of Clayton and Giauque,[15] Giauque and Clayton,[16] and Giauque

[13] F. R. Bichowsky and F. D. Rossini, *Thermochemistry* (Reinhold, 1936).

[14] *International Critical Tables.*

[15] J. D. Clayton and W. F. Giauque, J. Am. Chem. Soc. **54**, 2610 (1932), (βg-graphite).

[16] W. F. Giauque and J. O. Clayton, J. Am. Chem. Soc. **55**, 4875 (1933), (Nitrogen).

TABLE III. *The free energy function and heat contents of the ideal gases.*

	ClCN		BrCN		ICN		$(CN)_2$	
T°K	$-\left(\frac{F°-E_0°}{T}\right)$†	$(H°-E_0°)$††	$-\left(\frac{F°-E_0°}{T}\right)$	$(H°-E_0°)$	$-\left(\frac{F°-E_0°}{T}\right)$	$(H°-E_0°)$	$-\left(\frac{F°-E_0°}{T}\right)$	$(H°-E_0°)$
250	44.73	2.04	47.97	2.09	50.02	2.18	45.98	2.40
291.1		2.46		2.53		2.64		2.93
298.1	46.20	2.53	49.48	2.61	51.59	2.72	47.70	3.03
300	46.25	2.55	49.53	2.63	51.65	2.75		
350	47.59	3.10	50.92	3.20	53.09	3.33	49.40	3.75
400	48.80	3.67	52.32	3.79	54.39	3.93	50.87	4.48
500	50.90	4.85	54.33	5.00	56.64	5.17		
600	52.72	6.07	56.11	6.24	58.55	6.44		
700	54.30	7.35	57.83	7.53	60.23	7.73		
800	55.72	8.64	59.18	8.83	61.77	9.06		
900	57.01	9.96	60.59	10.17				
1000	58.20	11.31	61.82	11.53				
$S^0_{298.1}$	54.72 E.U.		58.26 E.U.		60.76 E.U.		57.90 E.U.	

† cal./mole degree.
†† kcal./mole.

and Overstreet,[17] we find

$$\Delta((F^\circ - E_0^\circ)/T)_{298.1} = -3.27 \text{ cal./mole degree.}$$
$$\Delta F^\circ = \Delta E_0^\circ + T\Delta((F^\circ - E_0^\circ)/T)$$

hence

$$C_{\beta g} + \tfrac{1}{2}N_2 + \tfrac{1}{2}Cl_2 = ClCN_{(g)},$$
$$\Delta F^\circ_{298.1} = 35.5 \text{ kcal./mole.}$$

From the Bichowsky and Rossini[13] heat of formation of crystalline ICN, and the heats of sublimation of I_2[18] and ICN[19] one finds,

$$C_{\beta g} + \tfrac{1}{2}N_2 + \tfrac{1}{2}I_{2(g)} = ICN_{(g)},$$
$$\Delta H_{291.1} = 45.80 \text{ kcal./mole,}$$
$$\Delta(H^\circ - E_0^\circ)_{291.1} = 0.22 \text{ kcal./mole,}$$

and thus

$$\Delta E_0^\circ = 45.6 \text{ kcal.,} \quad \Delta((F^\circ - E_0^\circ)/T)_{298.1} = -4.43 \text{ cal./mole degree.}$$

so we have

$$C_{\beta g} + \tfrac{1}{2}N_2 + \tfrac{1}{2}I_{2(g)} = ICN_{(g)},$$
$$\Delta F^\circ_{298.1} = 44.3 \text{ kcal./mole.}$$

Since $\tfrac{1}{2}I_{2(c)} = \tfrac{1}{2}I_{2(g)}$,
$$\Delta F^\circ_{298.1} = 2.32 \text{ kcal./mole,}[18]$$

$$C_{\beta g} + \tfrac{1}{2}N_2 + \tfrac{1}{2}I_{2(c)} = ICN_{(g)},$$
$$\Delta F^\circ_{298.1} = 46.6 \text{ kcal./mole.}$$

Yost and Stone[19] found from equilibrium measurements

$$C_{\beta g} + \tfrac{1}{2}N_2 + \tfrac{1}{2}I_{2(c)} = ICN_{(g)},$$
$$\Delta F^\circ_{298.1} = 45.94 \text{ kcal./mole.}$$

They used for the reaction $C_{\beta g} + \tfrac{1}{2}N_2 + \tfrac{1}{2}H_2 = HCN_{(g)}$, $\Delta F^\circ_{298.1} = 27.60$ kcal. If in place of this value, one uses Gordon's[20] value of 28.51 kcal. for the free energy of formation of HCN, the Yost and Stone Data give

$$C_{\beta g} + \tfrac{1}{2}N_2 + \tfrac{1}{2}I_{2(c)} = ICN_{(g)},$$
$$\Delta F^\circ_{298.1} = 46.85 \text{ kcal./mole}$$

in good agreement with the value obtained from the heat of formation. We may take as a final value for the free energy of formation of gaseous ICN, $\Delta F^\circ_{298.1} = 46.75$ kcal./mole.

Neither thermal nor equilibrium data are available for cyanogen bromide. Since $\Delta F^\circ_{298.1}$ for the formation of HBr[21] is within one kcal. equal to the mean of the free energy of formation of HCl[17] and HI[22] one may assume that the same would obtain for BrCN. One would thus predict that for

$$C_{\beta g} + \tfrac{1}{2}N_2 + \tfrac{1}{2}Br_{2(g)} = BrCN_{(g)},$$
$$\Delta F^\circ_{298.1} = 40 \text{ kcal./mole.}$$

The best value for the heat of formation of cyanogen is given as -71 kcal./mole by Bichowsky and Rossini.[13] This yields 71.07 kcal./mole for ΔE_0°. Thus we have from Table III and references 15 and 16

$$2C_{\beta g} + N_2 = (CN)_2, \quad \Delta F^\circ_{298.1} = 69.1 \text{ kcal./mole.}$$

This value is considerably different from that found by McMorris and Badger,[23] namely 60.1 kcal./mole. The reason for this discrepancy is that their value for the heat of formation of cyanogen is 8.00 kcal./mole smaller than that given by Bichowsky and Rossini. The Bichowsky and Rossini value is based primarily on the combustion results of von Wartenburg and Schütza[24] which were carefully corrected for the formation of NO during the combustion. McMorris and Badger failed to apply such a correction to their combustion data. The value found for $S^\circ_{298.1}$ for cyanogen 57.9 E.U. is in good agreement with that calculated by Badger and McMorris.[23] The heat capacity of gaseous cyanogen is being measured in this laboratory by Mr. Burcik in order to check the frequency assignment.

In conclusion I should like to thank Professor L. Pauling of this Institute and Dr. J. Y. Beach of Princeton University for permitting the use of the new values for the interatomic distances in cyanogen and cyanogen chloride and bromide, prior to their publication.

[17] W. F. Giauque and R. Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932), (Chlorine).
[18] W. F. Giauque, J. Am. Chem. Soc. **53**, 507 (1931).
[19] D. M. Yost and W. E. Stone, J. Am. Chem. Soc. **55**, 1889 (1933).
[20] A. R. Gordon, J. Chem. Phys. **5**, 30 (1937).
[21] A. R. Gordon and C. Barnes, J. Chem. Phys. **1**, 692 (1933).
[22] G. M. Murphy, J. Chem. Phys. **4**, 344 (1936).
[23] J. McMorris and R. M. Badger, J. Am. Chem. Soc. **55**, 1952 (1933).
[24] H. von Wartenburg and H. Schütza, Zeits. f. physik. Chemie **164A**, 386 (1933).

Electric Moment of Cellosolves

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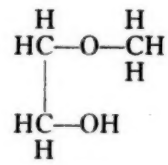
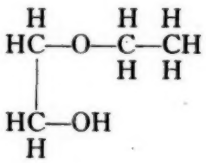
(Received October 17, 1938)

THE purpose of this investigation was the determination of the electric moments of some members of the series of compounds known by the trade name of "Cellosolves." These compounds seem to possess some very desirable properties as organic solvents. Three members of the series were investigated, namely;

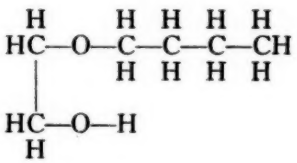
(1) Methyl Cellosolve—ethylene glycol mono-methyl ether.



(2) Cellosolve—ethylene glycol mono-ethyl ether.

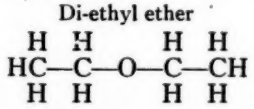


(3) Butyl Cellosolve—ethylene glycol mono-butyl ether.

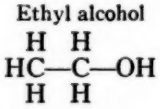


An examination of the structural formulae reveals that these compounds simultaneously resemble both ethers and alcohols.

Di-ethyl ether



Ethyl alcohol



It is this property which makes the Cellosolves excellent solvents. It seemed of interest to discover whether the series showed a dipole variation similar to that of the alcohols or similar to that of the ethers. The results obtained will be discussed from this point of view.

EXPERIMENTAL

To find the dipole moment the method of dilution of a polar solute in a nonpolar solvent was used. The molar polarization of such a mixture is given by:[1]

$$P_{12}=\frac{M_1f_1+M_2f_2}{d}\frac{\epsilon-1}{\epsilon+2}=P_1f_1+P_2f_2, \quad (1)$$

where f_1, f_2 and M_1, M_2 and P_1, P_2 are, respectively, the mole fraction, molecular weights, and polarizations of the components; d is the density and ϵ the dielectric constant of the mixture. If one of the two substances is polar and the other is nonpolar, the polarization of the mixture may be found by Eq. (1) for various concentrations and the value extrapolated to correspond to infinite dilution of the polar component. The electric moment of the polar component is given by:

$$\mu=0.0127\times10^{-18}((P-P_0)T)^{\frac{1}{2}}, \quad (2)$$

where P is the molar polarization of the substance, P_0 is its molar refraction, and T is the absolute temperature. This method was used for determining the electric moment of the Cellosolves. Benzene was used as the nonpolar solvent.

The quantities to be determined experimentally are the dielectric constant and density of each mixture; and the refractive index and density of the pure polar liquid. The densities were determined by the pycnometer method with an accuracy of 0.1 percent. The dielectric constants were found to an accuracy of 0.2 percent from the capacities of a test condenser in air and filled with the various solutions. The capacities were found by the substitution method using a Hartley oscillating circuit. The Hartley

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[1] P. Debye, *Polar Molecules* (Chemical Catalog Company, New York, 1929).

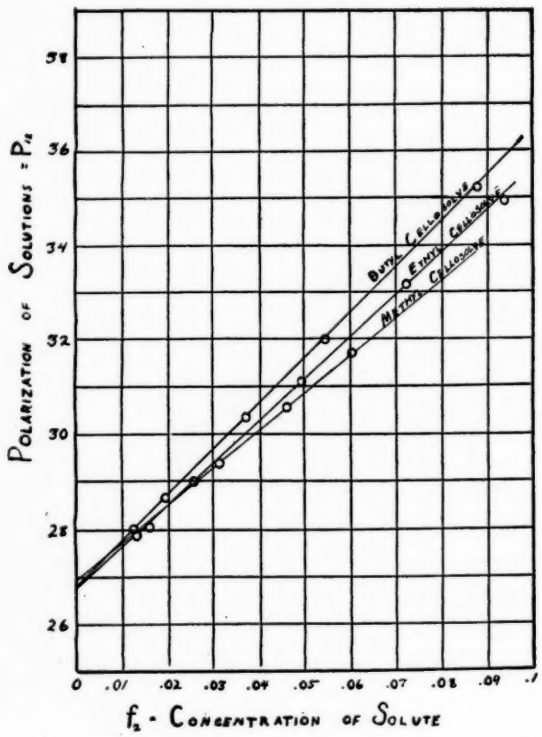

FIG. 1.

oscillator containing the test condenser and a General Radio precision condenser in parallel beat against a crystal oscillator. A vernier condenser, similar to one used previously in the laboratory,[2] was connected in parallel with the precision condenser to allow fine adjustments. The oscillations of the crystal set were kept at a constant frequency of 1470 kc by means of piezoelectric crystal. The beat note was kept at 1000 cycles by eliminating the pulsations between it and the note of an electrically driven tuning fork of that frequency. Thus the frequency of the Hartley oscillator could be returned to the same value with the test condenser in and out of the circuit by adjusting the precision and vernier condensers. The dielectric constant of the mixture in the test condenser was found following the method of Davies[3] to eliminate the effect of the capacities of the leads.

The test condenser used consisted of two concentric nickel-plated, brass cylinders. The inner cylinder was supported from the inside by a closely fitting glass tube, while the outer cylinder was supported from the outside by another glass tube. These two glass tubes were joined together at the base about 2 cm below the brass cylinders and formed the container for the liquid whose dielectric constant was to be measured. This arrangement eliminated all solid dielectric between the plates of the condenser. The air capacity of the condenser was 49.02 mmf.

The data obtained for methyl, ethyl, and butyl Cellosolve are given in Tables I, II, III, respectively.

In Fig. 1, P_{12} is plotted against f_2. The value of electric moments were found by use of these curves and Eq. (2). The results appear in Table IV. The probable error in these results is 0.6 percent.

CONCLUSION

Reference to values obtained and given in Table IV, and the values for the alcohols and

TABLE I. *Methyl Cellosolve in benzene, mean temperature 25°C.**

f_2	ϵ	d	P_{12}
0.0159	2.370	0.8722	28.04
0.0313	2.470	0.8733	29.37
0.0460	2.566	0.8740	30.59
0.0602	2.657	0.8748	31.70
0.1285	3.204	0.8804	37.40

* Density of benzene, 0.8717; density of methyl Cellosolve, 0.9596; refractive index of methyl Cellosolve, 1.399.

TABLE II. *Cellosolve in benzene, mean temperature 25°C.**

f_2	ϵ	d	P_{12}
0.0130	2.354	0.8717	27.90
0.0256	2.431	0.8727	29.00
0.0494	2.581	0.8727	31.10
0.0726	2.740	0.8737	33.15
0.0942	2.888	0.8749	34.96

* Density of benzene, 0.8717; density of Cellosolve, 0.9229; refractive index of Cellosolve, 1.405.

TABLE III. *Butyl Cellosolve in benzene, mean temperature 24°C.**

f_2	ϵ	d	P_{12}
0.0191	2.393	0.8728	28.63
0.0371	2.500	0.8732	30.36
0.0548	2.605	0.8736	32.01
0.0882	2.818	0.8744	35.21
0.1192	3.017	0.8752	38.05

* Density of benzene, 0.8717; density of butyl Cellosolve, 0.8968; refractive index of butyl Cellosolve, 1.416.

[2] J. F. Payne, "Effect of X-rays on Dielectric Constant," Thesis, University of Florida (1935).
[3] R. M. Davies, Phil. Mag. **21**, 1–41 (1936).

symmetrical ethers quoted in Table V reveals that the Cellosolves behave very similarly to the alcohols in respect to variation of electric moment and not at all like the symmetrical ethers. This is shown graphically in Fig. 2. The most plausible explanation is given by Smyth[4] for the case of water and the alcohols. Similarly, when a hydrogen atom in ethylene glycol is replaced by a methyl group to form methyl Cellosolve, a considerable decrease in electric moment occurs. Smyth and Walls[5] assume the angle which the resultant moment of each half of the glycol molecule makes with the C−C bond to be nearly 90°. In methyl Cellosolve this angle is increased by increased repulsion between the methyl and the remaining hydrogen; so that the moment of methyl Cellosolve (2.04×10^{-18}) is less than that of ethylene glycol (2.3×10^{-18}). The further substitution of an ethyl or butyl group for the methyl apparently causes little change in the angle for there is no increase in bulk in the immediate neighborhood of the hydrogen. So after the initial decrease in moment from ethylene glycol to methyl Cellosolve, the moments of the Cellosolves remain sensibly constant. It is not surprising that the ethers behave differently, since they are symmetrical. The author was unable to find values for the electric moments of the unsymmetrical ethers; but from the manner in which they increase in complexity, one would expect that their moments would vary in the manner of the Cellosolves and alcohols. This problem deserves investigation.

TABLE IV.

COMPOUND	ELECTRIC MOMENT $\times10^{18}$
Ethylene Glycol	2.3*
Methyl Cellosolve	2.04
Cellosolve	2.08
Butyl Cellosolve	2.08

* C. P. Smyth, *Dielectric Constant and Molecular Structure* (Chemical Catalog Company, New York, 1931).

TABLE V.*

COMPOUND	ELECTRIC MOMENT $\times10^{18}$
Water	1.85
Methyl alcohol	1.68
Ethyl alcohol	1.70
n-propyl alcohol	1.66
n-butyl alcohol	1.65
Methyl ether	1.29
Ethyl ether	1.12
Propyl ether	0.86

* See footnote to Table IV.

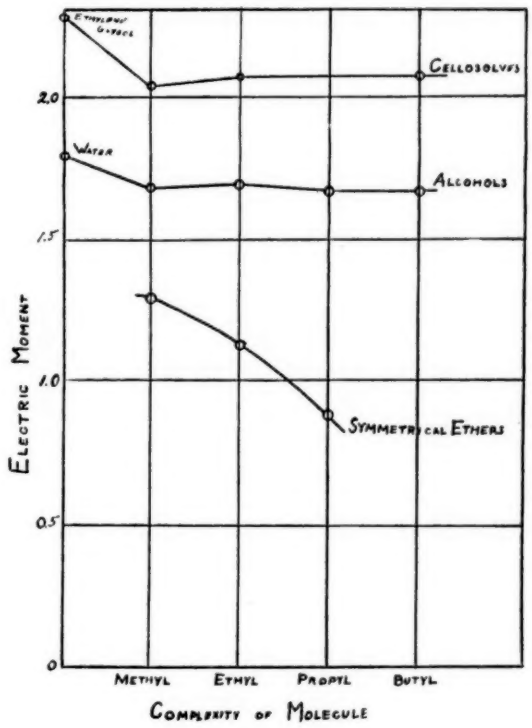

FIG. 2.

The author is indebted to the Carbon and Carbide Corporation for the samples of the Cellosolves supplied. He also wishes to take this opportunity to express his appreciation to Dr. A. A. Bless without whose direction this investigation would have been impossible.

[4] C. P. Smyth, *Dielectric Constant and Molecular Structure* (Chemical Catalog Company, New York, 1931), Chapter V.

[5] C. P. Smyth and W. S. Walls, J. Am. Chem. Soc. **53**, 2115 (1931).

The Potential Function of the Acetylene Molecule. I.

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(Received December 7, 1938)

A perturbation calculation is made of the anharmonicity coefficients in the vibrational energy expression of C_2H_2 in terms of the constants in the most general first-order and second-order perturbing potentials consistent with the geometrical symmetry of the molecule. From an analysis of the absorption spectrum, a tentative classification is made and the anharmonicity coefficients and the zeroth-order frequencies are calculated. The zeroth-order potential constants so obtained are: $k_{CH}=6.24$, $k_{CC}=17.2$, $k_{CCH}=-0.67$ in 10^5 dynes/cm, compared with the values $k_{CH}=5.85$, $k_{CC}=15.6$, $k_{CCH}=0.028$ obtained by using the observed frequencies. In the appendix the relation between bond constants and molecular structure is discussed.

INTRODUCTION

RECENTLY the potential constants of molecules have been the subject of many investigations. Besides furnishing informations concerning the general structure of the molecules, the potential constants obtained from the vibrational spectra may throw light on such questions as the existence of resonance between two or more possible structures and the nature of the electronic state of certain chemical bonds. Such constants, however, as calculated from the infrared absorption and the Raman frequencies are subject to uncertainties arising from (1) the anharmonicity in the vibrations, and (2) the indefiniteness inherent in the ambiguity in the choice of the potential function of a molecule. The effect of anharmonicity may be expected to be large in the case of molecules containing light atoms such as hydrogen. It has been shown by Bonner[1] that the observed frequencies of the water molecule differ from the zeroth-order frequencies by about five percent and the O−H bond constant calculated with the observed frequencies can be shown to differ from the zeroth-order constants by about ten percent. Unfortunately, only in the case of a few molecules are enough bands known to permit a determination of the zeroth-order potential constants.

The acetylene molecule C_2H_2 containing the C−H and the C≡C bonds is of considerable interest since the force constants of these bonds are often used for comparison with those of similar bonds in other molecules. The infra-red and the photographic regions of the spectrum have been thoroughly investigated by a number of authors.[2–5] Classifications of the absorption bands have been given by Sutherland,[6] Herzberg,[3] and by Mecke.[4] The force constants of the molecule have been calculated by Colby[7] from the observed frequencies. The purpose of this paper is to carry out a perturbation calculation of the anharmonicity coefficients in the energy expression in terms of the constants in the first- and the second-order potentials (i.e., cubic and quartic in the coordinates), and eventually to determine these potentials from the experimental values of the anharmonicity coefficients.

CLASSICAL TREATMENT

As the starting point of the perturbation calculation, we shall follow Colby's classical treatment of the normal vibrations of the molecule. As there is no mechanical coupling between the parallel or valence vibrations and the perpendicular or deformation vibrations, and as the electrical coupling between these two types of vibrations is probably small, we may treat them separately in the zeroth approximation. For the

* At present at Kun-ming.

[1] L. G. Bonner, Phys. Rev. **45**, 496; **46**, 458 (1934).

[2] For references to earlier work, see for example H. A. Stuart, *Molekulstruktur*.

[3] G. Herzberg and J. W. T. Spinks, Zeits. f. Physik **91**, 386 (1934); G. Herzberg, F. Patat and H. Verleger, *ibid.* **102**, 1 (1936).

[4] R. Mecke, Zeits. f. Physik **99**, 217 (1936); R. Mecke and R. Ziegler, *ibid.* **101**, 405 (1936).

[5] G. W. Funke and G. Herzberg, Phys. Rev. **49**, 100 (1936); G. W. Funke, Zeits. f. Physik **99**, 341 (1936); **104**, 169 (1937); G. W. Funke and E. Lindholm, *ibid.* **106**, 518 (1937).

[6] G. B. B. M. Sutherland, Phys. Rev. **43**, 883 (1933).

[7] W. F. Colby, Phys. Rev. **47**, 388 (1935).

parallel vibrations, let the relative displacements between two neighboring atoms in the order H−C≡C−H be x_1, x_2, x_3. The kinetic energy T is given by

$$2T=\frac{m(m+M)}{\Sigma}(\dot{x}_1^2+\dot{x}_3^2)+\frac{(m+M)}{2}\dot{x}_2^2 +m(\dot{x}_1+\dot{x}_3)\dot{x}_2+\frac{2m^2}{\Sigma}\dot{x}_1\dot{x}_3, \quad (1)$$

where $\Sigma=2(M+m)$; and the potential energy consistent with the symmetry of the molecule is

$$2V=k_1(x_1^2+x_3^2)+k_2x_2^2 +2k_3(x_1+x_3)x_2+2k_4x_1x_3. \quad (2)$$

The determinantal equation gives for the symmetrical vibrations

$$\lambda_1+\lambda_2=\frac{\Sigma}{2mM}(k_1+k_4)+\frac{2}{m}(k_2-2k_3), \qquad \lambda_1\cdot\lambda_2=\frac{2}{mM}[(k_1+k_4)k_2-2k_3^2] \quad (3)$$

and for the antisymmetrical vibration

$$\lambda_3=\frac{m+M}{mM}(k_1-k_4), \quad (4)$$

where $\lambda_i=4\pi^2\nu_i^2$. Let the normal coordinates of the vibrations ν_1, ν_2, ν_3 be Q_1, Q_2, Q_3, respectively. Then

$$x_i=\sum_{k=1}^{3}c_{ik}Q_k, \quad (5)$$

where c_{ik} is proportional to the value of the minor of the ith element in any row of the determinant of (1) and (2) in which λ is given the value $\lambda_k=4\pi^2\nu_k^2$. It follows from (3) and (4) that

$$c_{11}=c_{31}, \quad c_{12}=c_{32}, \quad c_{13}=-c_{33}, \quad c_{23}=0. \quad (6)$$

Accordingly the forms of vibrations are as shown in Fig. 1.

For the perpendicular vibrations, instead of the angles between two neighboring bonds, we shall choose for convenience in later calculations the coordinates R_1 and R_2 defined as follows.

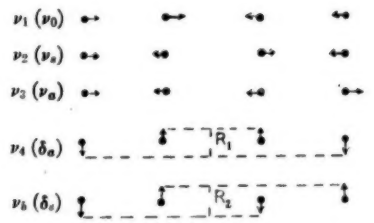

FIG. 1.

Let the displacements of the H, C, C, H atoms perpendicular to the axis be z_1, z_2, z_3, z_4, respectively. Then

$$2R_1=(z_1+z_4)-(z_2+z_3), \qquad 2(a+b)R_2=[bz_1+(2a+b)z_3]-[bz_4+(2a+b)z_2], \quad (7)$$

where a is the C−H distance and b is the C≡C distance. In these coordinates, the kinetic energy is

$$2T=\mu_1\dot{R}_1^2+\mu_2\dot{R}_2^2, \quad (8)$$

where

$$\mu_1=\frac{2mM}{m+M}, \quad \mu_2=\frac{2mM(a+b)^2}{Mb^2+m(2a+b)^2}.$$

As the potential energy must be symmetrical with respect to the line of centers, the quadratic potential must be of the form

$$2V=C_1R_1^2+C_2R_2^2. \quad (9)$$

The determinantal equation gives for the antisymmetrical and the symmetrical (with respect to the center of symmetry) vibrations ν_4 and ν_5

$$\mu_1\lambda_4=C_1, \quad \mu_2\lambda_5=C_2. \quad (10)$$

For C_2H_2, $\nu_4\backsimeq730$ cm^{-1}, $\nu_5\backsimeq605$ cm^{-1}, $a=1.06\times10^{-8}$ cm, $b=1.19\times10^{-8}$ cm. Hence

$$C_1=0.58, \quad C_2=0.946 \quad \text{in } 10^5 \text{ dynes/cm}.$$

With these values for the constants C_1 and C_2, one obtains for deuteroacetylene C_2D_2 from (3) and (4)

$$\nu_4\backsimeq536 \text{ cm}^{-1}, \quad \nu_5\backsimeq506 \text{ cm}^{-1}$$

in agreement with Colby's values.[7] This is to be expected, as the coordinates R_1, R_2 are in fact proportional to the normal coordinates into which Colby's angles would transform.

Perturbation Calculation

The kinetic energy of vibration of C_2H_2 is given by

$$2T=\dot{Q}_1^2+\dot{Q}_2^2+\dot{Q}_3^2+\mu_1(\dot{R}_1^2+R_1^2\dot{\varphi}_1^2)+\mu_2(\dot{R}_2^2+R_2^2\dot{\varphi}_2^2),$$

where φ_1, φ_2 are the angles which R_1, R_2 make, respectively, with a fixed direction perpendicular to the axis and passing through the center of gravity of the molecule. The zeroth-order potential energy is, from (2) and (9),

$$2V_0=\lambda_1Q_1^2+\lambda_2Q_2^2+\lambda_3Q_3^2+C_1R_1^2+C_2R_2^2.$$

On introducing the dimensionless coordinates

$$y_i=2\pi(\omega_i/h)^{\frac{1}{2}}Q_i,\quad i=1,2,3,\quad \sigma=2\pi(\omega_4\mu_1/h)^{\frac{1}{2}}R_1,\quad \rho=2\pi(\omega_5\mu_2/h)^{\frac{1}{2}}R_2 \tag{11}$$

and the momenta $p_i=\partial T/\partial\dot{q}_i$, one obtains

$$\begin{aligned}T&=(2\pi^2/h)[\omega_1p_1^2+\omega_2p_2^2+\omega_3p_3^2+\omega_4(p_\sigma^2+(1/\sigma^2)p_{\varphi_1}^2)+\omega_5(p_\rho^2+(1/\rho^2)p_{\varphi_2}^2)],\\ V_0&=\tfrac{1}{2}h[\omega_1y_1^2+\omega_2y_2^2+\omega_3y_3^2+\omega_4\sigma^2+\omega_5\rho^2],\end{aligned} \tag{12}$$

where the ω's are the frequencies of the normal vibrations. The Schrödinger equation $(T+V_0)\Psi=E\Psi$ may be solved by the usual method of separation of variables, namely,

$$\Psi_{v_1v_2v_3v_4l_1v_5l_2}=\psi_{v_1}(y_1)\psi_{v_2}(y_2)\psi_{v_3}(y_3)\psi_{v_4l_1}(\sigma_1\varphi_1)\psi_{v_5l_2}(\rho_1\varphi_2)$$

and

$$E_0=\sum_i E^{v_i}.$$

The $\psi_v(y)$, $\psi_{vl}(\sigma,\varphi)$ are the well-known normalized orthogonal functions

$$\psi_v(y)=\frac{1}{(\sqrt{\pi}2^v v!)^{\frac{1}{2}}}e^{-y^2/2}H_v(y),\quad H_v(y)=(-1)^v e^{y^2}\frac{d^ve^{-y^2}}{dy^v},$$

$$\psi_{vl}(\sigma,\varphi)=\frac{\sqrt{k!}}{(l+k)^{\frac{1}{2}}}\frac{1}{\sqrt{\pi}}e^{\pm il\varphi}\sigma^l e^{-\sigma^2/2}L_{l+k}^{\,l}(\sigma^2),$$

where $k=(v-l)/2$, and $L_{l+k}^{\,l}(\sigma^2)$ is the associated Laguerre polynomial of argument σ^2. The energy E_0 is given by

$$E_0/h=\omega_1(v_1+\tfrac{1}{2})+\omega_2(v_2+\tfrac{1}{2})+\omega_3(v_3+\tfrac{1}{2})+\omega_4(v_4+1)+\omega_5(v_5+1). \tag{13}$$

Let us now introduce the first- and the second-order perturbing potentials which are consistent with the symmetry of the molecule, namely, they must be symmetrical with respect to the center of the molecule and motions must be isotropic in planes perpendicular to the axis. Hence they must be even functions of y_3, R_1 and R_2, and must be independent of φ_1 and φ_2. Thus

$$V_1=h[ay_1^3+by_2^3+cy_1^2y_2+dy_1y_2^2+ey_1y_3^2+fy_1\sigma^2+gy_1\rho^2+iy_2y_3^2+jy_2\sigma^2+ky_2\rho^2], \tag{14}$$

$$\begin{aligned}V_2=h[&\beta_1y_1^4+\beta_2y_2^4+\beta_3y_3^4+\beta_4\sigma^4+\beta_5\rho^4+\beta_6y_1^2y_2^2+\beta_7y_1^2y_3^2+\beta_8y_1^2\sigma^2+\beta_9y_1^2\rho^2+\beta_{10}y_2^2y_3^2\\&+\beta_{11}y_2^2\sigma^2+\beta_{12}y_2^2\rho^2+\beta_{13}y_3^2\sigma^2+\beta_{14}y_3^2\rho^2+\beta_{15}\sigma^2\rho^2+\beta_{16}y_1^3y_2+\beta_{17}y_1y_2^3\\&+\beta_{18}y_1y_2y_3^2+\beta_{19}y_1y_2\sigma^2+\beta_{20}y_1y_2\rho^2].\end{aligned} \tag{15}$$

The first-order energy change E_1 is zero as the diagonal elements of V_1 are zero on account of the properties of the zeroth-order wave functions. The second-order energy change E_2 is given by

$$E_2=(V_2)_{v^v}+\sum_{v'}{}'[(V_1)_{v^{v'}}]^2/[E_0^{\,v}-E_0^{\,v'}], \tag{16}$$

where v and v' stand for the totality of the quantum numbers v_1, v_2, v_3, v_4, l_1, v_5, l_2 and v_1', v_2', v_3', v_4', l_1', v_5', l_2', respectively;

$$(V_2)_v{}^v=\int|\Psi_v|^2V_2d\tau,\quad (V_1)_v{}^{v'}=\int\Psi_{v'}{}^*V_1\Psi_v d\tau,\quad d\tau=dy_1dy_2dy_3\sigma d\sigma d\varphi_1\rho d\rho d\varphi_2$$

and the summation is taken over all possible sets of v' for which $(V_1)_v{}^{v'}$ does not vanish. All the diagonal elements of V_2 and the nonvanishing, nondiagonal elements of V_1 can be readily calculated. While the most general form for the second-order potential contains 20 terms, it can be seen that the contributions from the last five terms in (15) to E_2 are zero. The nondiagonal elements of V_1 contribute 40 terms to E_2.[8] A straight-forward calculation gives the following expression for the total energy of the system

$$\begin{aligned}E=E_0+E_1+E_2=h[&x_0+\nu_1v_1+\nu_2v_2+\nu_3v_3+\nu_4v_4+\nu_5v_5+x_{11}v_1{}^2+x_{22}v_2{}^2+x_{33}v_3{}^2+x_{44}v_4{}^2+x_{55}v_5{}^2\\&+x_{l_1l_1}l_1{}^2+x_{l_2l_2}l_2{}^2+x_{12}v_1v_2+x_{13}v_1v_3+x_{14}v_1v_4+x_{15}v_1v_5+x_{23}v_2v_3+x_{24}v_2v_4+x_{25}v_2v_5\\&+x_{34}v_3v_4+x_{35}v_3v_5+x_{45}v_4v_5],\end{aligned}\tag{17}$$

where

$$\begin{aligned}x_0=&\tfrac{1}{2}(\omega_1+\omega_2+\omega_3)+\omega_4+\omega_5+\tfrac{3}{4}(\beta_1+\beta_2+\beta_3)+2(\beta_4+\beta_5)+\tfrac{1}{4}(\beta_6+\beta_7+\beta_8+\beta_9+\beta_{10})\\&+\tfrac{1}{2}(\beta_{11}+\beta_{12}+\beta_{13}+\beta_{14})+\beta_{15},\\
\nu_1=&\omega_1+\tfrac{1}{2}(3\beta_1+\beta_6+\beta_7)+\beta_8+\beta_9-\frac{3a}{\omega_1}\left[\frac{5}{4}a+\frac{d}{2}+\frac{e}{2}+f+g\right]-\frac{c}{2\omega_2}[3b+c+i+2j+2k]\\&-\frac{d^2}{4(\omega_1+2\omega_2)}+\frac{d^2}{4(\omega_1-2\omega_2)}-\frac{e^2}{4(\omega_1+2\omega_3)}+\frac{e^2}{4(\omega_1-2\omega_3)}-\frac{f^2}{2(\omega_1+2\omega_4)}+\frac{f^2}{2(\omega_1-2\omega_4)}\\&-\frac{g^2}{2(\omega_1+2\omega_5)}+\frac{g^2}{2(\omega_1-2\omega_5)}+\frac{c^2}{8(\omega_2-2\omega_1)}-\frac{3c^2}{8(\omega_2+2\omega_1)},\\
\nu_2=&\omega_2+\tfrac{1}{2}(3\beta_2+\beta_6+\beta_{10})+\beta_{11}+\beta_{12}-\frac{3b}{\omega_2}\left[\frac{5}{4}b+\frac{e}{2}+\frac{i}{2}+j+k\right]-\frac{d}{2\omega_1}[3a+d+e+2f+2g]\\&-\frac{c^2}{4(\omega_2+2\omega_1)}+\frac{c^2}{4(\omega_2-2\omega_1)}-\frac{i^2}{4(\omega_2+2\omega_3)}+\frac{i^2}{4(\omega_2+2\omega_3)}-\frac{j^2}{2(\omega_2+2\omega_4)}+\frac{j^2}{2(\omega_2-2\omega_4)}\\&-\frac{k^2}{2(\omega_2+2\omega_5)}+\frac{k^2}{2(\omega_2-2\omega_5)}+\frac{d^2}{8(\omega_1-2\omega_2)}-\frac{3d^2}{8(\omega_1+2\omega_2)},\\
\nu_3=&\omega_3+\tfrac{1}{2}(3\beta_3+\beta_7+\beta_{10})+\beta_{13}+\beta_{14}-\frac{e}{2\omega_1}[3a+d+e+f+g]-\frac{i}{2\omega_2}[3b+c+i+j+k]\\&+\frac{e^2}{8(\omega_1-2\omega_3)}-\frac{3e^2}{8(\omega_1+2\omega_3)}+\frac{i^2}{8(\omega_2-2\omega_3)}-\frac{3i^2}{8(\omega_2+2\omega_3)},\end{aligned}\tag{18}$$

[8] The nonvanishing, nondiagonal elements of V_1 are the following:

$$(V_1)^{v_1\pm1\ v_2\ v_3\ v_4\ v_5}_{v_1\ v_2\ v_3\ v_4\ v_5}\quad (V_1)^{v_1\pm3\ v_2\ v_3\ v_4\ v_5}_{v_1\ v_2\ v_3\ v_4\ v_5}\quad (V_1)^{v_1\ v_2\pm1\ v_3\ v_4\ v_5}_{v_1\ v_2\ v_3\ v_4\ v_5}\quad (V_1)^{v_1\ v_2\pm3\ v_3\ v_4\ v_5}_{v_1\ v_2\ v_3\ v_4\ v_5}$$

$$(V_1)^{v_1\pm1\ v_2\pm2\ v_3\ v_4\ v_5}_{v_1\ v_2\ v_3\ v_4\ v_5}\quad (V_1)^{v_1\pm2\ v_2\pm1\ v_3\ v_4\ v_5}_{v_1\ v_2\ v_3\ v_4\ v_5}\quad (V_1)^{v_1\pm1\ v_2\ v_3\pm2\ v_4\ v_5}_{v_1\ v_2\ v_3\ v_4\ v_5}\quad (V_1)^{v_1\ v_2\pm1\ v_3\pm2\ v_4\ v_5}_{v_1\ v_2\ v_3\ v_4\ v_5}$$

$$(V_1)^{v_1\pm1\ v_2\ v_3\ v_4\pm2\ v_5}_{v_1\ v_2\ v_3\ v_4\ v_5}\quad (V_1)^{v_1\pm1\ v_2\ v_3\ v_4\ v_5\pm2}_{v_1\ v_2\ v_3\ v_4\ v_5}\quad (V_1)^{v_1\ v_2\pm1\ v_3\ v_4\pm2\ v_5}_{v_1\ v_2\ v_3\ v_4\ v_5}\quad (V_1)^{v_1\ v_2\pm1\ v_3\ v_4\ v_5\pm2}_{v_1\ v_2\ v_3\ v_4\ v_5},$$

where $l_1'=l_1$, $l_2'=l_2$ in all these matrix elements.

$$\nu_4=\omega_4+3\beta_4+\tfrac{1}{2}(\beta_8+\beta_{11}+\beta_{13})+\beta_{15}-\frac{j}{2\omega_2}(3b+c+i+2j+2k)-\frac{f}{2\omega_1}(3a+d+e+2f+2g)$$
$$-\frac{j^2}{2(\omega_2+2\omega_4)}-\frac{f^2}{2(\omega_1+2\omega_4)},$$

$$\nu_5=\omega_5+3\beta_5+\tfrac{1}{2}(\beta_9+\beta_{12}+\beta_{14})+\beta_{15}-\frac{k}{2\omega_2}(3b+c+i+2j+2k)-\frac{g}{2\omega_1}(3a+d+c+2f+2g)$$
$$-\frac{k^2}{2(\omega_2+2\omega_5)}-\frac{g^2}{2(\omega_1+2\omega_5)},$$

$$x_{11}=\tfrac{3}{2}\beta_1-\frac{15a^2}{4\omega_1}-\frac{c^2}{2\omega_2}-\frac{c^2}{8(\omega_2+2\omega_1)}-\frac{c^2}{8(\omega_2-2\omega_1)},$$

$$x_{22}=\tfrac{3}{2}\beta_2-\frac{15b^2}{4\omega_2}-\frac{d^2}{2\omega_1}-\frac{d^2}{8(\omega_1+2\omega_2)}-\frac{d^2}{8(\omega_1-2\omega_2)},$$

$$x_{33}=\tfrac{3}{2}\beta_3-\frac{e^2}{2\omega_1}-\frac{i^2}{2\omega_2}-\frac{e^2}{8(\omega_1+2\omega_3)}-\frac{e^2}{8(\omega_1-2\omega_3)}-\frac{i^2}{8(\omega_2+2\omega_3)}-\frac{i^2}{8(\omega_2-2\omega_3)},$$

$$x_{44}=\tfrac{3}{2}\beta_4-\frac{f^2}{2\omega_1}-\frac{j^2}{2\omega_2}-\frac{f^2}{8(\omega_1+2\omega_4)}-\frac{f^2}{8(\omega_1-2\omega_4)}-\frac{j^2}{8(\omega_2+2\omega_4)}-\frac{j^2}{8(\omega_2-2\omega_4)},$$

$$x_{55}=\tfrac{3}{2}\beta_5-\frac{g^2}{2\omega_1}-\frac{k^2}{2\omega_2}-\frac{g^2}{8(\omega_1+2\omega_5)}-\frac{g^2}{8(\omega_1-2\omega_5)}-\frac{k^2}{8(\omega_2+2\omega_5)}-\frac{k^2}{8(\omega_2-2\omega_5)},$$

$$x_{l_1l_1}=-x_{44}+\beta_4-\frac{f^2}{2\omega_1}-\frac{j^2}{2\omega_2},$$

$$x_{l_2l_2}=-x_{55}+\beta_5-\frac{g^2}{2\omega_1}-\frac{k^2}{2\omega_2},$$

$$x_{12}=\beta_6-\frac{3ad}{\omega_1}-\frac{3bc}{\omega_2}-\frac{d^2}{2(\omega_1+2\omega_2)}+\frac{d^2}{2(\omega_1-2\omega_2)}-\frac{c^2}{2(\omega_2+2\omega_1)}+\frac{c^2}{2(\omega_2-2\omega_1)},$$

$$x_{13}=\beta_7-\frac{3ae}{\omega_1}-\frac{ci}{\omega_2}-\frac{e^2}{2(\omega_1+2\omega_3)}+\frac{e^2}{2(\omega_1-2\omega_3)},$$

$$x_{23}=\beta_{10}-\frac{de}{\omega_1}-\frac{3bi}{\omega_2}-\frac{i^2}{2(\omega_2+2\omega_3)}+\frac{i^2}{2(\omega_2-2\omega_3)},$$

$$x_{14}=\beta_8-\frac{3af}{\omega_1}-\frac{cj}{\omega_2}-\frac{f^2}{2(\omega_1+2\omega_4)}+\frac{f^2}{2(\omega_1-2\omega_4)},$$

$$x_{15}=\beta_9-\frac{3ag}{\omega_1}-\frac{ck}{\omega_2}-\frac{g^2}{2(\omega_1+2\omega_5)}+\frac{g^2}{2(\omega_1-2\omega_5)},$$

$$x_{24}=\beta_{11}-\frac{df}{\omega_1}-\frac{3bj}{\omega_2}-\frac{j^2}{2(\omega_2+2\omega_4)}+\frac{j^2}{2(\omega_2-2\omega_4)},$$

$$x_{25}=\beta_{12}-\frac{dg}{\omega_1}-\frac{3bk}{\omega_2}-\frac{k^2}{2(\omega_2+2\omega_5)}+\frac{k^2}{2(\omega_2-2\omega_5)},$$

$$x_{34}=\beta_{13}-\frac{ef}{\omega_1}-\frac{ij}{\omega_2},$$

$$x_{35}=\beta_{14}-\frac{eg}{\omega_1}-\frac{ik}{\omega_2},$$

$$x_{45}=\beta_{15}-\frac{fg}{\omega_1}-\frac{jk}{\omega_2}.$$

From these one obtains on elimination

$$\begin{aligned}
\omega_1&=\nu_1-x_{11}-\tfrac{1}{2}x_{12}-\tfrac{1}{2}x_{13}-x_{14}-x_{15},\\
\omega_2&=\nu_2-x_{22}-\tfrac{1}{2}x_{12}-\tfrac{1}{2}x_{23}-x_{24}-x_{25},\\
\omega_3&=\nu_3-x_{33}-\tfrac{1}{2}x_{13}-\tfrac{1}{2}x_{23}-x_{34}-x_{35},\\
\omega_4&=\nu_4-2x_{44}-\tfrac{1}{2}x_{14}-\tfrac{1}{2}x_{24}-\tfrac{1}{2}x_{34}-x_{45},\\
\omega_5&=\nu_5-2x_{55}-\tfrac{1}{2}x_{15}-\tfrac{1}{2}x_{25}-\tfrac{1}{2}x_{35}-x_{45}.
\end{aligned}\qquad(19)$$

If all the 22 quantities ν_1, ν_2, ν_3, $\cdots$ x_{35}, x_{45} are known from an analysis of the experimental data, Eqs. (18) and (19) may be regarded as a system of 17 independent equations for 25 unknown constants a, b, $\cdots$ j, k, β_1, $\beta_2\cdots\beta_{15}$. A rigorous solution of these equations is hence not possible. However, as an approximation, we may discard some of the terms in (14) and (15) which are expected to be small on consideration of the empirical data. Such a calculation depends on an accurate determination of the quantities ν_1, ν_2, ν_3, $\cdots$ x_{35}, x_{45} and will be given in the second part of this paper.

Zeroth-Order Frequencies and Potential Constants

For the calculation of the potential constants, one needs the zeroth-order frequencies which must be obtained from the Eqs. (19). The determination of the coefficients ν_1, ν_2, $\cdots$ x_{11}, $\cdots$ x_{45} depends on the classification of the observed bands in the spectrum. Sutherland[6] gave a classification of most of the bands known up to that time on considerations of their intensities and the selection rules of Dennison.[9] Herzberg and his co-workers[3] gave another classification which differs from that of Sutherland chiefly in interchanging the assignments $3\nu_a=9835$, $\nu_a+2\nu_s=9640$ cm^{-1} of Sutherland. With Herzberg's values for the coefficients ν_1, ν_2, $\cdots$ x_{45}, the agreement between the calculated frequencies and the observed frequencies is not satisfactory for most of the bands. Mecke and Ziegler,[4] on considering ν_a, ν_s and δ_a, δ_s as two pairs of degenerate vibrations, gave another classification in which a vibrational level is defined by three principal quantum numbers for the C−H, C≡C and the deformation vibrations, and two auxiliar quantum numbers. The agreement obtained between the calculated and the observed frequencies is very satisfactory for the majority of the bands. It can be shown, however, that resonance interactions between two vibrations of different symmetry characters, such as the symmetrical ν_s and the antisymmetrical ν_a, do not arise. In the case of the two deformation vibrations, it can be shown that the energy change arising from the resonance interaction is very small and of the order of $\sim$1 cm^{-1}.[10] Hence an

[9] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[10] These statements follow from considerations similar to that of D. M. Dennison on CO_2, Phys. Rev. **41**, 304 (1932). For the two valence C−H vibrations ν_s and ν_a, let us assume in the zeroth approximation $\omega_2=\omega_3$, and in the first approximation $\omega_2=\omega_3+\Delta$. From (12) and (14) one finds for that part of the first-order Hamiltonian which is a function of the coordinates y_2 and y_3

$$H_1'=\frac{h\Delta}{2}\left[-\frac{\partial^2}{\partial y_2^2}+y_2^2\right]+hiy_2y_3^2.$$

It can easily be shown that the secular determinants giving the energies of the states for given values of the sum $\nu_2+\nu_3$ are diagonal. For the deformation vibrations δ_s and δ_a, let us assume in the zeroth approximation $\omega_4=\omega_5$ and in the first approximation $\omega_4=\omega_5+\Delta$. Then that part of the Hamiltonian that is a function of the coordinates ρ and σ is

$$H'=\frac{h\Delta}{2}\left[p_\sigma^2+\frac{1}{\sigma^2}p_{\varphi_1}^2+\sigma^2\right]+h\beta_{15}\sigma^2\rho^2.$$

Simple calculation from the secular equations for the states $v_4+v_5=0, 1, 2, 3$ gives the following energies:

v_5	v_4	E'/h	
0	3	$3\Delta+5\beta_{15}+(\Delta^2-2\Delta\beta_{15}+3\beta_{15}^2)^{\frac{1}{2}}$	2188.2
1	2	$2\Delta+5\beta_{15}+(\Delta^2+2\Delta\beta_{15}+3\beta_{15}^2)^{\frac{1}{2}}$	2046.6
2	1	$3\Delta+5\beta_{15}-(\Delta^2-2\Delta\beta_{15}+3\beta_{15}^2)^{\frac{1}{2}}$	1927.2
3	0	$2\Delta+5\beta_{15}-(\Delta^2+2\Delta\beta_{15}+3\beta_{15}^2)^{\frac{1}{2}}$	1834.6
0	2	$2\Delta+3\beta_{15}+(\Delta^2+\beta_{15}^2)^{\frac{1}{2}}$	1458.8
1	1	$2\Delta+4\beta_{15}$	1328.8
2	0	$2\Delta+3\beta_{15}-(\Delta^2+\beta_{15}^2)^{\frac{1}{2}}$	1222.8
0	1	$2\Delta+2\beta_{15}$	729
1	0	$\Delta+2\beta_{15}$	612
0	0	$\Delta+\beta_{15}$	0.

As $0\,0\rightarrow1\,0=612$ cm^{-1}, and $0\,0\rightarrow0\,1=729$ cm^{-1}, $0\,0\rightarrow1\,1=1328.6$ cm^{-1}, one obtains

$$\Delta=117\text{ cm}^{-1}$$
$$\beta_{15}=-12.4\text{ cm}^{-1}.$$

With these values of Δ and β_{15}, one obtains the energies in

unambiguous assignment of seven quantum numbers v_1, v_2, v_3, v_4, l_1, v_5, l_2 to each vibrational level is still possible, and a classification in accordance with the selection rules is desirable. In Table I we suggest such a classification which is an extension of that of Sutherland. For the purpose of comparison we also include that classification of the photographic bands by Funke and Lindholm[5] according to Mecke and Ziegler's system.

In the classification suggested here, the bands marked by an asterisk are those employed in the calculation of the coefficients $\nu_1, \nu_2, \nu_3, \cdots x_{35}, x_{45}$. It is seen that the calculated and the observed frequencies of the rest of the bands agree fairly well, although in a few cases they differ by as much as 80 cm^{-1}. These bands are high combination bands and their assignments may be uncertain. As similar discrepancies are also found in Funke and Lindholm's assignment according to Mecke and Ziegler's system, these may not be a particularly serious objection against our classification.[11] On assuming the assignment here, we obtain the following tentative set of values for the coefficients in (18)

$$\begin{aligned}
&\nu_1=1984,\ x_{11}=-11,\ x_{12}=-3,\quad x_{24}=-9,\\
&\nu_2=3421,\ x_{22}=-49,\ x_{13}=-9,\quad x_{25}=-11,\\
&\nu_3=3293,\ x_{33}=-5,\quad x_{14}=10,\quad x_{34}=0,\\
&\nu_4=\ ?\ ,\ x_{44}=\ ?\ ,\ x_{15}=-25,\quad x_{35}=-18,\\
&\nu_5=602,\quad x_{55}=-11,\ x_{23}=-149,\ x_{45}=-13,\\
&\nu_4+x_{44}=729.
\end{aligned} \tag{20}$$

The ν_4 and x_{44} cannot be determined until a band is known to involve some harmonics of ν_4. With these values for the coefficients, the zeroth-order frequencies according to (19) are

$$\omega_1=2016,\quad \omega_2=3565,\quad \omega_3=3393,\quad \omega_4=?,\quad \omega_5=622. \tag{21}$$

With these zeroth-order frequencies, it is possible to calculate the zeroth-order potential constants in (2). On neglecting the term in k_4 which represents the interaction between the two extreme atoms and is certainly very small, one finds

$$k_{CH}=6.24,\quad k_{CC}=17.2,\quad k_3=-0.67 \tag{22}$$

in 10^5 dynes/cm, as compared with the values

$$k_{CH}=5.85,\quad k_{CC}=15.59,\quad k_3=0.028 \tag{22a}$$

obtained by Colby with the observed frequencies uncorrected for anharmonicity. It is seen that differences as great as ten percent in the values of the bond constants may result from using the observed instead of the true frequencies. A similar calculation of the zeroth-order potential constants of HCN shows that the C−H bond constant is also about 6.2×10^5 as compared with the value 5.66×10^5 obtained with the

TABLE I. *Vibrational spectrum of* C_2H_2.

ASSIGNMENT SUGGESTED	ν CM^{-1} CALC.	ν CM^{-1} AND BAND TYPE OBS.	ν CM^{-1} CALC.	ASSIGNMENT OF FUNKE
ν_a	3288*	3288 ∥		1_1a 0 0
ν_s	3372*	3372 Ra		1_1s 0 0
$3\nu_a$	9835*	9835 ∥		3_1a 0 0
$\nu_a+\nu_s$	6513	6500 ∥		2_2a 0 0
$\nu_a+2\nu_s$	9640*	9640 ∥	9638	3_2a 0 0
$\nu_a+3\nu_s$	12670	12675 ∥	12678	4_4a 0 0
$\nu_a+4\nu_s$	15600*	15600 ∥	15600	5_5a 0 0
$\nu_a+5\nu_s$	18433	18430 ∥	18424	6_6a 0 0
$\nu_a+\nu_0$	5250*	5250 ∥		1_1a 1 0
$3\nu_a+\nu_0$	11781	11783 ∥	11781	3_1a 1 0
$\nu_a+\nu_s+\nu_0$	8474	8450? ∥		2_2a 1 0
$\nu_a+2\nu_s+\nu_0$	11600*	11600 ∥	11587	3_2a 1 0
$\nu_a+3\nu_s+\nu_0$	14624	14617 ∥		4_4a 1 0
$\nu_a+4\nu_s+\nu_0$	17552	17519 ∥	17533	5_5a 1 0
$\nu_a+2\nu_s+2\nu_0$	13534	13532.4∥	13526	3_2a 2 0
$\nu_a+\delta_s$	3882*	3882 ⊥		1_1a 0 1_1s
$\nu_s+\delta_a$	4092*	4092 ⊥		1_1s 0 1_1a
$\delta_a+\delta_s$	1328.6*	1328.6∥		0 0 2_0a
$\nu_s+\delta_a+\delta_s$	4680	4690 ∥		1_1s 0 2_0a
$\nu_a+2\nu_s+\delta_s-\delta_s$	9601	9603 ∥		3_2a 0 1_1s←0 0 1_1s
$\nu_a+3\nu_s+\delta_s-\delta_s$	12620	12618 ∥		4_4a 0 1_1s←0 0 1_1s
$\nu_a+4\nu_s+\delta_s-\delta_s$	15539	15521 ∥	15539	5_5a 0 1_1s←0 0 1_1s
$3\nu_a+\delta_s-\delta_s$	9781	9801 ∥		3_1a 0 1_1s←0 0 1_1s
ν_0	1973*	1973 Ra		0 1 0
δ_s	612*	612 Ra		0 0 1_1s
δ_a	729*	729 ⊥		0 0 1_1a
$2\nu_a+\nu_s+\delta_a$	10364*	10364 ⊥	10351	3_2s 0 1_1a
$3\nu_a+\delta_s$	10394	10413 ⊥	10409	3_2a 0 1_1s
$\nu_a+3\nu_s+\delta_s$	13230*	13230 ⊥	13240	4_4a 0 1_1s
$2\nu_a+\nu_0+\delta_a+\delta_s$	9906*	9906 ∦	9921	2_0s 1 2_0a
$3\nu_s+\nu_0+\delta_a+\delta_s$	13039	13033 ∥	13034	4_2a 0 0
$2\nu_a+\nu_0+\delta_a+\delta_s$	9745*	9745 ∥	9709	2_2s 1 2_0a
$2\nu_a+2\nu_0+\delta_a+\delta_s$	11663*	11663 ∥	11632	2_2s 2 2_0a
$\nu_a+2\nu_s+\nu_0+2\delta_s$	12711*	12711 ∥	12704	3_2a 1 2_2s
$\nu_a+2\nu_s+2\nu_0+2\delta_s$	14597*	14597 ∥	14618	3_2a 2 2_2s
$\nu_0+\delta_a+\delta_s$	3286	3294 ∥		0 1 2_0a
$\nu_a+\nu_s+\nu_0+2\delta_s$	9614	9668 ∥		2_2a 1 2_2s
$\nu_a+\nu_s+2\nu_0+2\delta_s$	11510	11570 ∥	11577	2_2a 2 2_2s
$\nu_0+\delta_a$	2712	2702 ⊥		0 1 1_1a
$2\nu_s+\nu_0+\delta_a$	9343	9366 ⊥		2_0s 1 1_1a
$\nu_a+\nu_s+\nu_0+\delta_s$	9057	9085 ⊥	9087	2_2a 1 1_1s
$\nu_a+3\nu_s+\nu_0+\delta_s$	15160	15081 ⊥	15169	4_4a 1 1_1s
$\nu_a+4\nu_s+\nu_0+\delta_s$	18077	18088 ⊥	18072	5_5a 1 1_1s
$2\nu_a+\nu_0+\delta_a$	9260	9177 ⊥		2_2s 1 1_1a
$\nu_a+3\nu_0$	9114	9151 ∦		1_1a 3 0
$\nu_s+3\nu_0+\delta_a+3\delta_s$	11565	11586 ∥	11566	1_1s 3 4_2a
$\nu_s+3\nu_0+\delta_a+5\delta_s$	12731	12732.7∥	12632	1_1s 3 6_4a

the table. It is seen that the levels $n\nu_5$ and $n\nu_4$ differ respectively from $612n$ and $729n$ only by about 1 cm^{-1}, and the level $m\nu_5+n\nu_4$ differs from $612m+729m$ by $mn\beta_{15}$, which is really the second-order energy in (17) and (18).

[11] It may be noticed that while the differences between the observed and our calculated values for the 9366 and 9085 cm^{-1} bands are of the order of 30 cm^{-1}, there are similar differences in the case of the 9745 and 11663 cm^{-1} bands in Funke and Lindholm's assignment. For the 15081 cm^{-1} band, the discrepancy is about the same in both assignments, while for the 12732.7 cm^{-1} band, our assignment seems definitely better.

TABLE II. *Potential constants of C_2Cl_4 in 10^5 dynes/cm. See references mentioned for their definitions.*

	(1)	(2)	(3)	(4)
k_{CC}	6.15	6.81	6.19	6.81
$k_{CCl}+k_3$			4.9	4.6
a	4.59	4.70		
b	1.89	1.94		
d	1.52	1.62		
e	——	0.29		

observed frequencies.[12] That the C−H bond constant is the same in C_2H_2 and HCN indicates an identical electronic structure in the C−H bonds of these molecules, but the considerably lower values of the C−H bond constants in CH_4 and molecules containing the methyl group CH_3 namely, $\sim 5.0\times 10^5$, probably correspond to a different electronic structure, as pointed out by Sutherland and Dennison.[13] In view, however, of the corrections brought about by effect of anharmonicity, it seems that in general one may not attach too much significance to the exact values of the force constants ordinarily calculated with the observed frequencies, and that one may not base conclusions concerning such effects as resonance and electronic structure solely on small differences (less than ten percent) between the force constants in different molecules.

APPENDIX

Bond Constants and Molecular Structure

That resonance between two or more possible structures should reveal itself in the values of the bond constants is most definitely established in the following cases: Benzene, where the C−C bond constant is 7.5×10^5;[14] carbon dioxide in which the C−O bond constant is $\sim 15.9\times 10^5$;[15] carbon suboxide in which the C−C constant is $\sim 12.5\times 10^5$ and the C−O constant is $\sim 16.0\times 10^5$;[16] and tetrachlorethylene in which the C−C constant is about 6.8×10^5. In these cases, the anharmonicity corrections may be expected to be small, and the differences of the bond constants from their "normal" values are great enough to justify the conclusion concerning the existence of resonance. Even then, we can only regard the bond constants as certain within ~ 10 percent, because of the ununiqueness in the choice of the potential potential. For example, Table II gives the potential constants of C_2Cl_4 calculated (1) by Duchesne[17] with Sutherland and Dennison's potential,[13] (2) with the same potential but with the interaction between the Cl atoms in one CCl_2 group and the C atom of the other group partially taken into account by including a term $2e(x_1+x_2)x_0$ in the potential, (3) by Thompson and Linnett[18] with a valence force potential, and (4) with the slightly different valence force potential of Wilson given in the paper of Bonner.[19]

Among the cases where difference in the electronic state is definitely revealed in the values of the bond constants, in addition to the C−H bonds in C_2H_2, HCN and the methyl group already mentioned, and possibly the N=N bond in azomethane as suggested by West and Killingsworth,[20] we may mention the C−C bond in diacetylene C_4H_2. The valence bond constants of this molecule have been calculated from the infra-red and the Raman frequencies by Wu and Shen.[21] The C−C constant is 3.58×10^5 which is considerably lower than the C−C constant in C_2H_6, namely, $\sim 5\times 10^5$. This low value is due to the low Raman frequency 644 cm^{-1} and it was at first thought that this frequency may not be a fundamental symmetrical valence vibration of the molecule. Recent observations, however, of Woo and Chu[22] on the ultraviolet absorption spectrum of the molecule show that certain bands with the frequency difference ~ 640 cm^{-1} are relatively intensified by raising the temperature of the gas. This leaves no doubt that the frequency 644 cm^{-1} is a fundamental frequency of the normal electronic state of the molecule. Thus the low C−C constant is real. This considerably weaker binding of the C−C bond in C_4H_2 is consistent with the observed ease with which the molecule is dissociated compared with ethane. It cannot be caused by resonance in this case, since the binding would be strength-

[12] The zeroth-order frequencies of the two parallel vibrations of HCN can be calculated from the recent data of E. Lindholm, Zeits. f. Physik **108**, 454 (1938),

$$\omega_1 = \nu_1 - x_{11} - x_{12} - \tfrac{1}{2}x_{13} = 2000.0$$
$$\omega_3 = \nu_2 - x_{33} - x_{23} - \tfrac{1}{2}x_{13} = 3450.4.$$

From these,

$k_{CH}=6.30$,	$k_{CN}=16.2$,	for k_{HCN} assumed to be 0
6.24	16.4	−0.3
6.17	16.6	−0.6

as compared with the values

$$k_{CH}=5.66,\quad k_{CN}=18.1,\quad k_{HCN}=-0.3$$

obtained by P. F. Bartunek and E. F. Barker, Phys. Rev. **48**, 376 (1935). Although the values of k_{CH}, k_{CN} are uncertain because of the unknown value of the interaction term k_{HCN}, it can be seen that for reasonable values of k_{HCN}, the values of k_{CH} and k_{CN} differ from those calculated with the observed frequencies by ~ 10 percent.

[13] G. B. B. M. Sutherland and D. M. Dennison, Proc. Roy. Soc. **A148**, 250 (1935).

[14] See for example K. W. F. Kohlrausch, Physik. Zeits. **37**, 58 (1936).

[15] Obtained with the zeroth-order frequencies $\omega_1=1361$, $\omega_3=2397$.

[16] Obtained with the equations of H. W. Thompson and J. W. Linnett, J. Chem. Soc. 1291 (1937), and the Raman frequencies 843, 2160 for the symmetrical valence vibrations and the infra-red frequencies 1570, 2290 obtained by R. C. Lord and N. Wright, J. Chem. Phys. **5**, 642 (1937). The constants obtained here differ somewhat from those of H. W. Thompson and J. W. Linnett, Nature **140**, 1065 (1937).

[17] J. Duchesne, Nature **139**, 288, 634 (1937).

[18] J. W. Thompson and J. W. Linnett, J. Chem. Soc. P. 1393 (1937).

[19] L. G. Bonner, J. Am. Chem. Soc. **58**, 34 (1936).

[20] W. West and R. B. Killingsworth, J. Chem. Phys. **6**, 1 (1938).

[21] T. Y. Wu and S. T. Shen, Chin. J. Phys. **2**, 128 (1936). This paper contains a few numerical errors. The C−C constant should be 3.58×10^5 instead of 2.85×10^5; also $k_3=0.71\times 10^5$ instead of 1.38×10^5.

[22] S. C. Woo and T. C. Chu, J. Chem. Phys. **5**, 786 (1937).

ened rather than weakened in this C−C bond by the resonance. It is probable that the electronic state of the C−C bond corresponds to an excited state with a weaker binding. In this case, one is not justified in assuming the same C−C bond constant for C_4H_2 as for C_2H_6 in the calculation of the frequencies of the normal vibrations of C_4H_2, as is done by Glockler and Wall.[23]

[23] G. Glockler and F. T. Wall, J. Chem. Phys. **5**, 813 (1937).

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Film Potentials of Stearate Multilayers and Other Dielectrics on Metal Surfaces

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A considerable amount of evidence is presented for the view that a part, if not all, of the film potential of an X multilayer of calcium stearate on a subphase of metal is due to a surface charge on the dielectric and a resultant induced charge in the metal. With a Y multilayer of an even number of layers, the potential, and therefore presumably the charge, is practically zero. This may indicate that the surface of the multilayer becomes charged only when it moves through the surface of the solution without the deposition of a new layer. There is some experimental evidence that the charge is less when the X multilayer moves upward through the monolayer of calcium stearate under no pressure than when it moves upward with the monolayer under pressure. The potential cannot be due to an equal charge deposited on and retained by every layer, since this indicates a film potential $\Delta V=4\pi netN(N+1)/2\epsilon$ increasing nearly as the square of the number of layers. The experiments indicate when X layers are deposited directly on the metal a variation as the first power, or $\Delta V=4\pi neNt/\epsilon$, which suggests a charge on the outer surface only. While Porter and Wyman find that if X layers are deposited upon a subphase of $(X+Y)$ layers, the second X layer gives a very much smaller potential increment than the first (increments of 2.7, 0.06, 0.8, 0.8, 0.7, 0.35 and 0.35 volt), we obtain a much more constant value on stearic acid (0.248, 0.300, 0.271, 0.259) and on paraffin (0.769, 0.911, 0.900, 1.085 and 1.085, also on thicker paraffin 5.0 volts for the first and 6.0 volts for the second X layer). The above results do not agree with equations developed for either a constant charge on the outer X layer only, or upon every X layer. The film potential is found to be a function of the pH, and of the nature of the positive ions, of the subsolution. Experiments on the effects of α- and γ-rays are described. In general we have found that the potential relations of multilayers are much more complicated than is indicated by the work of others, but this is due to the fact that the conditions of deposition have been varied to a greater extent. The effect of electrolysis upon the contact potential of gold and the film potential of paraffin on gold, has been investigated. These phenomena are also complicated, so only a few of the results with aluminum chloride as the solute, are described.

1. INTRODUCTION

WHEN two plates of metal are placed with their faces a short distance apart, a potential may be recorded by a compensating method provided[1] the inner face of one of them is coated with polonium, as in the Righi-Kelvin method, or[2] one of the plates is caused to vibrate at the rate of a few hundreds or thousands of vibrations per second, as in the method of Zisman. This latter method has been used by us to determine the potential of multilayers of calcium and other stearates.

It has been found by Blodgett and Langmuir[3] that calcium stearate monolayers may be transferred from the surface of an aqueous solution to that of a solid. At certain high values of the pH of the solution the deposition on the solid occurs only on the down trip (X films), and at certain lower values on both the down and up trips (Y films).

Porter and Wyman[4] have found that multilayers of the Y type deposited on a slide of metal

[1] Sir William Thomson, Lord Kelvin, *Mathematical and Physical Papers, Vol. VI, Contact Electricity of Metals* (Cambridge Press, 1911), pp. 110 to 145; M. Righi, J. de Phys. (2), **7**, 153 (1888).

[2] W. A. Zisman, Rev. Sci. Inst. **3**, 367 (1932); W. A. Zisman and H. G. Yamins, Physics **4**, 7 (1933); H. G. Yamins and W. A. Zisman, J. Chem. Phys. **1**, 656 (1933).

[3] (a) K. B. Blodgett, J. Am. Chem. Soc. **57**, 1007 (1935); (b) K. B. Blodgett and I. Langmuir, Phys. Rev. **51**, 964 (1937).

[4] E. F. Porter and P. Wyman, J. Am. Chem. Soc. **59**, 2746 (1937); **60**, 1083 (1938).

give by the method of Zisman a very low apparent contact potential, while the potential exhibited by X multilayers is nearly proportional to the number of layers, and of the order of 60 mv per layer.

According to Langmuir's initial hypothesis the molecules of all the layers in an X film are oriented with the polar group toward the surface of the metal, while in Y films the alternate layers have their molecules oriented in opposite directions. That this is not the true picture seems to be indicated by the work of Holley and Bernstein[5] who found that the spacing of the calcium or barium ions is practically the same in both types of film. Porter and Wyman conclude that there is a difference in orientations in the outer layer, but not in the other layers, provided the total number of layers is even, but that the X and Y multilayers with an odd number of layers have the same structure.

In a recent theoretical paper Langmuir[6] has expressed a conclusion stated in the following words:

"The progressively increasing contact potentials observed by Porter and Wyman during the building up of calcium stearate multilayers of type-X on alkaline solutions seem to be due to a surface charge on the uppermost monolayer rather than to the presence of dipole molecules within the film."

While in reaching this conclusion Langmuir had available the data in the second paper of Porter and Wyman, these were not available to us. However we were led to a somewhat similar but not identical conclusion from some of the striking experimental results given in the present paper, and the idea that a surface charge is involved was presented in a letter to the *Physical Review*.[7]

While both Langmuir's and our own earlier theory agreed in attributing the apparent contact potential to surface charges, they are both very indefinite as to the location and magnitude of the charge, and also give no evidence as to whether or not other factors are involved. It seems of importance therefore to present the experimental results upon which our letter was based, and to develop certain equations, fundamental to the theory, not considered by Langmuir. A considerable amount of the experimental work is of a different type from that of Porter and Wyman; other experiments agree with theirs in a qualitative sense, but are very different in a quantitative sense. We frequently obtain increments of 100 mv per X layer, while their maximum is of the order of 62 mv.

2. Dipole Theory of Multilayer Potentials

The surface potentials associated with *monolayers on water* seem to have their origin in the dipoles of the molecules in the film.

If it is assumed that the potentials developed in multilayers are also due to the dipoles present, the following relations would be expected to hold. The potential of a Y multilayer should be approximately zero if the total number of layers is even.

With an X multilayer, if all the dipoles were oriented in the same direction, in agreement with the earliest theory of these films, the potential should be additive. The potential should change by

$$\Delta V = 4\pi\tau/\epsilon \tag{1}$$

for each double layer if all the like charges lie in a plane parallel to the surface of the metal. If n is the number of molecules per sq. cm, each with a single dipole, and μ_p is the component of the dipole moment of each molecule perpendicular to the surface of the plane metal plate, then

$$\tau = n\mu_p, \tag{2}$$

$$\Delta V = 4\pi n\mu_p/\epsilon \tag{3}$$

or

$$\Delta V = 4\pi N n\mu_p/\epsilon, \tag{4}$$

where N is the number of layers on the metal plate. If the film were built of pure stearic acid, where the area per molecule is about 20A^2, and if we assume μ_p to be $1.4(10)^{-18}$ e.s.u.$\times$cm, then Eq. (4), the film potential increment, would be 1.0 volt per layer, if the dipoles were perpendicular to the surface, and if no charges are on the surface.

[5] C. Holley and S. Bernstein, Phys. Rev. **52**, 525 (1937).
[6] I. Langmuir, J. Am. Chem. Soc. **60**, 1190 (1938).
[7] W. D. Harkins and R. W. Mattoon, Phys. Rev. **53**, 911 (1938).

3. Charge Theory of Multilayer Potentials

Let it be supposed that when any single X layer is deposited on the down trip of the slide it collects no charge, but that on the upward movement, when no film is deposited, the outer surface of the X layer takes up a positive charge. This would produce an induced charge in the surface of the metal on which the layer is deposited. The general Gauss-Poisson equation for the potential is $\nabla^2 V = -4\pi\rho/\epsilon$ or for a condenser which consists of two equally charged parallel plates,

$$\Delta V = 4\pi neT/\epsilon, \tag{5}$$

in which n is the number of unit charges per sq. cm, e is the electronic charge, T is the total thickness of the dielectric (X layers, paraffin, etc.), and ϵ is the dielectric constant of the dielectric under the plane of the charge. Thus if all of the charge of a multilayer is associated with the outer layer only,

$$\Delta V = 4\pi neNt/\epsilon, \tag{6}$$

where t is the constant thickness of each X layer, and N is the total number of X layers.

If, however, an equal charge is deposited on each X layer and persists, then the potential will rise much more rapidly than with the first power of the thickness, which is contrary to a part of the experimental results presented later. The relation for equal charges retained on the surface of every layer is

$$\Delta V = 4\pi netN(N+1)/2\epsilon, \tag{7}$$

where ne is the surface density of the charge, t is the thickness of each X layer, and N is the total number of X layers. Thus if one X layer increases ΔV by 0.1 volt, then 20 X layers would give a potential of 21 volts. Experimentally, 20 X layers give a potential of about two volts.

The relations are modified if X layers are deposited upon a dielectric which covers the metal. Two different distributions of charge are considered below.

(1) A definite charge, whose value is independent of the thickness of the initial dielectric and of the X multilayer, is present on the outside layer only. For simplicity the thickness (T) of the dielectric is represented by $T = Mt$, where t is the average thickness of the X layers in a multilayer. The dielectric constant of the dielectric is ϵ_D and that of the X multilayer ϵ. Then

$$\Delta V = 4\pi net(M/\epsilon_D + N/\epsilon). \tag{8}$$

(2) A charge of a certain constant value remains upon every layer of the X multilayer. Then

$$\Delta V = 4\pi nel\left[\frac{NM}{\epsilon_D} + \frac{N(N+1)}{2\epsilon}\right]. \tag{9}$$

It is evident that if each X layer is to retain its charge and if the multilayer is deposited directly on the metal, the charge must decrease rapidly with the distance from the metal if the film potential is to be proportional to the number of X layers. Thus to meet this condition the charges on successive layers must be $\rho/1$, $\rho/2$, $\rho/3, \cdots \rho/N$.

The difference in the potential increments according to Eqs. (8) and (9) are illustrated by listing the potentials calculated for the case in which the thickness of the initial paraffin layer is equal to that of 100 X layers and the potential increment by Eq. (6) is 0.1 volt per layer. For simplicity the dielectric constants of the paraffin and the X multilayer are supposed to be the same. Actually that of the paraffin is somewhat lower.

Number of X layers =	1	2	3	4	5	6	7	8	9	10
ΔV if charge on outer layer only	10.1	10.2	10.3	10.4	10.5	10.6	10.7	10.8	10.9	11.0
ΔV if charge on every layer	10.1	20.3	30.6	41.0	51.5	62.1	72.8	83.6	94.5	105.5

4. Aqueous Subsolutions Used in Building Multilayers

Since the experiments described later seem to indicate that the film potential is dependent upon the pH of the subsolution and the nature of the positive ions present, it is important to know the characteristics of the aqueous solutions used in building both the X and Y multilayers. The composition of the solutions, together with the values of the film potentials obtained by their use, are given in Table I. In cases in which ammonium hydroxide is used without a buffer,

the *p*H decreases rapidly with time, and its value in the surface becomes much lower than that in the liquid.

5. Film Technique

All films were built at room temperature using regular methods[3a] at the pressure of castor oil (17 dynes/cm). An automatic mechanical dipping mechanism was used with a Pyrex tray.[8] The conductivity water was redistilled in an all-Pyrex still of special design. The stearic acid was recrystallized several times to increase its purity. The *X* films were always kept under the surface for 35 sec. between each down and up trip to obtain better films. Most of the *X* films were deposited on pure solid polished gold slides measuring 7.3×1.3×0.025 cm. Gold was used since its surface contact potential changes much less with accidental contamination than that of other metals. All measurements denoted by ΔV mean that the potential of the base metal was algebraically subtracted from the film potentials.

[8] R. W. Mattoon and S. Bernstein, Rev. Sci. Inst. **9**, 125 (1938).

6. Potential of the *Y* Type Multilayers

In agreement with the dipole theory, it has been found that the potential of a *Y* multilayer is small and does not increase with thickness. In our experiments the *Y* film potentials were even lower than those found by Porter and Wyman. For example, with 144, 160, 180 and 190 single *Y* layers the film potentials were respectively 7, 88, −27, and 2 mv, or practically zero.

Table I. *Composition of solutions and film potentials.*

Solution	Composition	Total No. of Layers	Slope mv/layer	Average
	For Building *X* Films (*p*H = 9.4)			
1.	10^{-4} m $CaCl_2$+NH_4OH	10	104	
		5	108	106
2.	10^{-4} m $CaCl_2$+10^{-4} m NH_4Cl+NH_4OH	20	95	
		30	95	
		30	89	
		30	86	
		35	86	90
3.	10^{-4} m $CaCl_2$+10^{-3} m NH_4Cl+NH_4OH	40	91	91
4.	10^{-4} m $Ca(CH_3COO)_2 \cdot H_2O$+10^{-3} m $KHCO_3$+NH_4OH	20	75	75
5.	10^{-4} m $Ca(CH_3COO)_2 \cdot H_2O$+$3(10)^{-3}$ m $KHCO_3$+NH_4OH	20	95	
		20	91	
		30	89	92
6.	10^{-4} m $Ca(CH_3COO)_2 \cdot H_2O$+$3(10)^{-3}$ m $KHCO_3$+KOH	20	56	
		30	59	58
7.	10^{-4} m $CaCl_2$+10^{-4} m $N(C_2H_5)_4Cl$+NH_4OH	40	82	
		40	87	85
	Solutions For Building *X* Films (*p*H = 6)			
8.	$3(10)^{-5}$ m $Pb(NO_3)_2$	27	5	5*
9.	10^{-4} m $AgNO_3$	34	−10	−10*
	Solution For Building *Y* Films (*p*H = 7.0)			
10.	$3(10)^{-5}$ m $BaCl_2 \cdot 2H_2O$+$3(10)^{-4}$ m $KHCO_3$	144	0.05	
		160	0.55	
		180	−0.15	
		190	0.01	0.11*

* Almost all of the potential of these films appears in the first few layers.

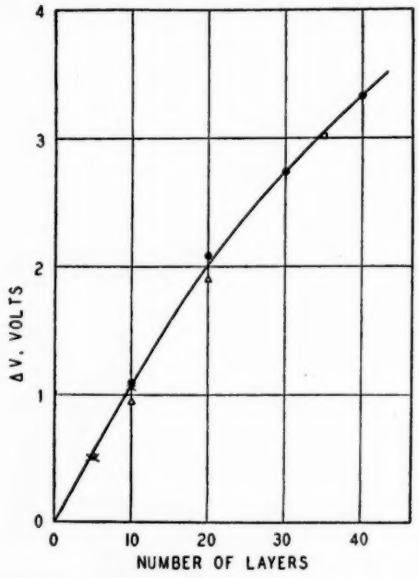

FIG. 1. Film potentials of five different X multilayers on gold made from solutions 1(O, X), 2(△, □), and 3(●). The potential increment is about 100 mv/layer up to 20 layers.

7. POTENTIAL OF X TYPE MULTILAYERS AND EFFECT OF THE COMPOSITION OF THE SUBSOLUTION

Up to thicknesses of 20 layers the increment of potential obtained in X multilayers of calcium stearate was found, for five different films produced by the use of solutions 1, 2, or 3, all of which contain ammonium hydroxide, to be 100 mv per layer. (Fig. 1.) This is 60 percent larger than the maximum obtained by Porter and Wyman. With solution 4 the increment was about 75 mv/layer, and with 5 about 90 mv/layer. Replacement of ammonium hydroxide by potassium hydroxide, as in solution 6, reduced the value to 58 mv/layer.

When the ammonium chloride of solution 2 was replaced by tetraethyl ammonium chloride of the same concentration the potential increment was lowered to 60, 82 and 87 mv/layer in three different experiments, while the thickness of the film was unchanged.

Langmuir[6] reports that a lead stearate X multilayer prepared by Miss Blodgett at a pH of 5.8 gave a negligible film potential, so he considers that the higher potentials of calcium stearate films are related to the higher values of the pH. In this laboratory Fourt has built multilayers of silver stearate with a decrement of 10 mv per layer, and lead with an increment of 5.4 mv, both at a pH of approximately 6. The effects of much smaller changes of pH are illustrated by Fig. 2. The initial pH (9.4) of the subsolution fell rapidly with time to 9.0 or less. It may be noted that so long as the pH did not fall too far from its initial value of 9.4, the film potential rose rapidly as the layers were deposited. However, at a lower pH the film potential began to fall rapidly. In each of the two cases represented in the figure the potential began to rise rapidly again as soon as the pH was raised from 9.0 or a little less to the initial value of 9.4. These results seem to indicate that the hydroxyl ion concentration of the solution is one of the most important factors in determining the increment of film potential.*

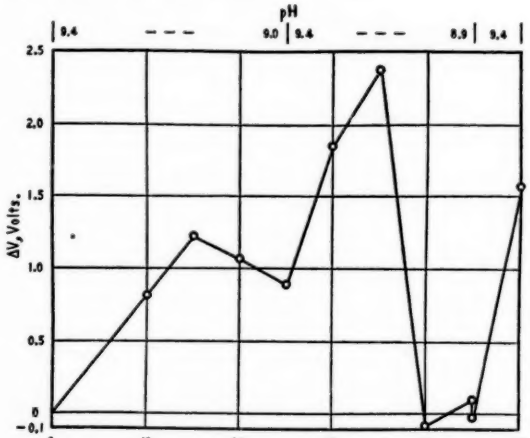

FIG. 2. Illustrates the effect of a lowering of pH in producing a rapid decrease of film potential. The pH in the surface of the subsolution decreases much more than the values listed for the pH indicate, since these values refer to the body of the subsolution. A restoration of the pH to 9.4 causes a rapid increase of film potential. (Solution 1 with calcium stearate.)

* *Note added Dec. 16.* A paper by J. J. Bikerman (Trans. Faraday Soc. **34**, 802 (1938)) indicates that the film potential is independent of pH. We have built calcium stearate films at a pH of 6.3 (R. W. Goranson and W. A. Zisman, Phys. Rev. **54**, 544 (1938)). Up to 40 layers only Y films deposited, but at 45 layers practically a pure X film was found to be depositing. The next five layers gave a total increment of only −40 mv, whereas at a pH 9.4 the value should have been of the order of +2000 mv. The next five layers gave a total increment of −20 mv. It should be noted that the lowering of the pH reduces the calcium stearate in the film to about 72 percent of the total stearate and stearic acid present. (I. Langmuir and V. Schaefer, J. Am. Chem. Soc. **58**, 285 (1936).) This and other similar experiments prove that such a reduction of pH eliminates practically the whole of the film potential.

The nature of the positive ions of the subsolution has an important influence. Thus we have obtained much higher potential increments than any other workers, but this has occurred only when ammonium or similar ions were employed, and these were not used by other investigators.

The increment of potential for each individual layer of a multilayer, is exhibited in Fig. 3.

8. Abnormal Potential Increments Obtained from *X* Layers

The first suggestion in our own work[7] that the potential of *X* multilayers is due to a surface charge was given by extreme abnormalities which appeared after the first 15 to 200 layers had been deposited. For example, the behavior of one such a film may be cited. This exhibited an entirely normal increment of potential (95 mv/layer) up to 40 layers (solution 3). Then rapid decreases and increases in film potential appeared, as shown in Fig. 4, even though no change had been made in the time of dipping, and the same subsolution had been used throughout.

In the deposition between 40 and 50 layers the *X* film, judged by the movement of the very short silk thread across a 6-cm gap in the barrier used as an indicator of the amount of film deposited, was added in an entirely normal amount on each down trip of the slide. Yet this deposition resulted in a mean decrement of potential of 290 mv per layer. Between 50 and 60 layers the amount of *X* film deposited on each down trip was less than the normal amount, and the potential decreased by only 10 mv per layer. Between 60 and 70 layers the amount of *X* film deposited was less than normal, but nevertheless the potential increased by 227 mv per layer, or more than twice as rapidly as the highest increment ever obtained for *X* films when they behave normally. Between 70 and 80 layers the *X* films deposited normally, yet the increment of 172 mv per layer was again abnormally high.

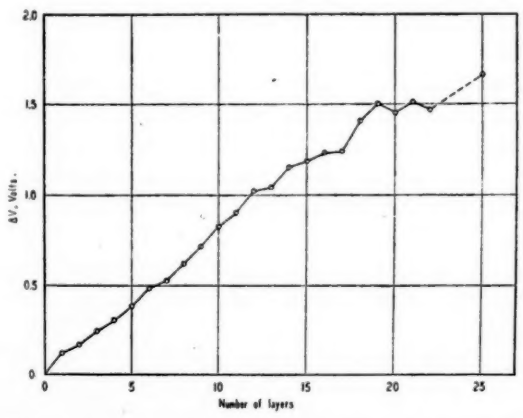

Fig. 3. Film potential for each of 22 single layers of an *X* film on gold (solution 4). Average slope 75 mv per layer.

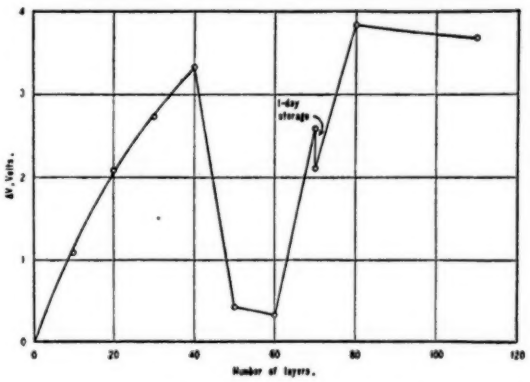

Fig. 4. Film potential of an *X* multilayer on gold (solution 3) exhibits abnormally rapid decreases and increases in potential at higher numbers of layers.

Such seemingly erratic behavior is much more easily explained on the basis of a surface charge produced by entangled or adsorbed ions than by the action of dipoles. This suggested that the rapid increase of potential due to *X* layer deposition after an abnormal decrease, is a result of the fact that the new *X* layers are deposited on a subphase of moderate thickness, while the initial *X* layers were deposited at the beginning almost on the metal. The abnormal effects described in this section seem to be practically absent from the work of Porter and Wyman. The discrepancy is probably due to differences in the subsolution, especially in the *p*H of its surface, and in the rate of deposition.

The property of the potential, in which it appears to endeavor to regain its normal value, just after it has experienced an abnormal loss, is of considerable interest. The above relations suggested that it would be important to determine the effect of depositing: (1) *Y* layers on an *X* multilayer; (2) *X* layers on a *Y* multilayer; (3) *X* layers on stearic acid deposited on gold by evaporation from a dilute solution; (4) *X* layers

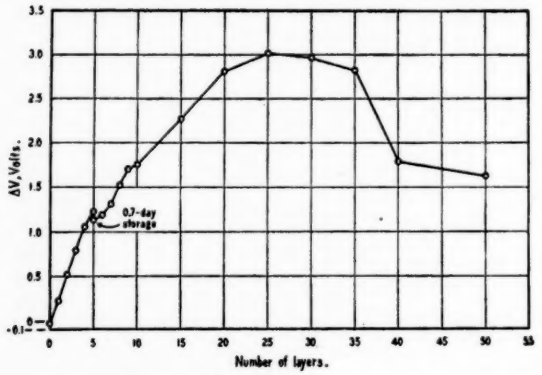

FIG. 5. Film potential of an X multilayer of calcium stearate (solution 5) deposited on a stearic acid layer (on gold) equivalent in thickness to a multilayer with 15 layers of calcium stearate. Average slope 250 mv per layer for the first 5 layers.

on various thicknesses of paraffin deposited on gold by solidification. Also (5) to determine the electrification of the surfaces of paraffin sheets of different thicknesses by dipping in mercury.

9. Effect of Y Layers on the Potential of an X Multilayer

Pairs of Y layers added to an X multilayer always quickly reduce the film potential to a value of from 0.1 v to about 0.4 v, irrespective of the magnitude of the X film potential. As a specific example, the addition of a single pair of Y layers reduced the potential of an X multilayer from 1.6 to 0.45 volt. In another series of four experiments the addition of two pairs of Y layers reduced the potentials of X films with only a small number of layers from 1.48 to 0.28 v, from 0.89 to 0.18 v, from 0.39 to 0.18 v, and from 0.20 to 0.16 volt. With more X layers and a higher film potential, Porter and Wyman have found a reduction to almost as low values.

10. X Layers on a Y Multilayer

If the potential of an X multilayer is due entirely to its constant surface charge associated entirely with the outer layer, then, Eq. (6), the potential of a single X layer on a Y multilayer should give a potential equal to that of an X multilayer of the same total thickness. However, if the Y multilayer contains many monolayers, additional X films should increase the potential only slightly. It was found that the

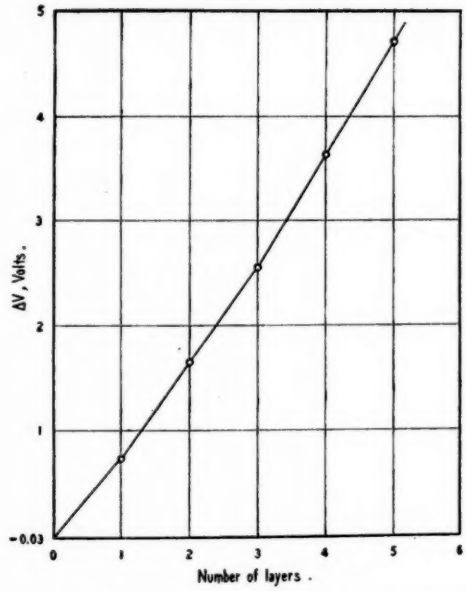

FIG. 6. Film potential of an X multilayer (solution 5) on a moderately thin sheet of paraffin on gold. Average slope 900 mv per layer.

addition of three X layers to a 180-layer Y film gave respectively 190, 590 and 420 mv, or a total of 1.2 volts, which is four times the ordinary increment for normal X films. However, Eq. (6) indicates that if the surface charge is the same, the potential for the first X layer added to a 180-layer Y film should be 181 times the normal X layer increment, or 18 volts. It might be supposed that the first layer does not take up the normal charge, because of some unknown abnormality in the structure, but even with three layers the total increment is small as compared with 18 volts. Therefore the idea that the charge on an X multilayer is in general of about the same magnitude, and is wholly on the outermost layer is not confirmed by these results. This same statement may be made on the basis of the data presented in Sections 11 and 12, which follow.

11. X Layers on a Subphase of Stearic Acid Deposited by Evaporation

A sheet of stearic acid, of an optical thickness equal to 15 monolayers of calcium stearate, was deposited on gold by evaporation from a very dilute solution in benzene. This sheet gave a very slightly negative potential (22 mv) but

five X layers deposited on it as a subphase gave potentials of 248, 300, 271, 259 and 173 mv, etc., as shown for every layer up to 10 in Fig. 5, or abnormally high values as compared with those obtained in the absence of the subphase of stearic acid.

12. X Layers on a Subphase of Paraffin

A moderately thin sheet of paraffin, deposited on gold by solidification of a thin liquid sheet, gave a very slightly negative potential of 30 mv (Fig. 6). This was presumably of a thickness between that represented by curves 1 and 2 in Fig. 7. Increments for the first five X layers deposited on top of this paraffin were 769, 911, 900, 1085 and 1085 mv per layer, or 4.75 volts for five X layers (Fig. 6). On a thicker paraffin sheet the increment was five volts for the first and six volts for the second X layer.

Later experiments are represented by Fig. 7. The values of the mean thickness ($\bar{t}$) of the paraffin sheets were obtained by weighing on an extremely sensitive balance and measuring the areas. With a film of 40μ thickness the first X layer increased the potential by 4.3 volts while with a mean thickness of 0.3μ (3000A) the increment for the first X layer was 135 mv. The mean thickness of this paraffin film corresponds to about 120 molecular layers of stearic acid, and interference colors were given by white light.

Irregularities in the thickness of these paraffin sheets make it impossible to exhibit the exact relation between thickness and potential, but it is evident that in general the potential for the first X layer increases with the thickness of the paraffin.

It is found that as the number of X layers deposited on either a stearic acid or a paraffin subphase is increased, the potential rises to a maximum and then decreases.

The thickness of the film and the potential may exhibit a considerable variation between the top and the bottom of the vertical metal plate. For example, a paraffin sheet of mean thickness 3000A gave, with 20 X layers added, a potential of 0.982 volt at the top and 1.826 volts at the bottom. This is due to a greater thickness at the bottom.

13. Potentials Induced by Dipping a Dielectric-Metal Sheet Through the Surface of Mercury

Goranson and Zisman[9] found that dipping an X film through a mercury surface gives a charge and a resultant potential to the surface of the X film. We have found that this induced potential is positive, and there is evidence that the first dip of a dielectric on metal through a mercury surface does more charging than succeeding dips. For example, the film potential of 200 X layers on chromium was reduced nearly to zero by the alpha-rays from polonium. Then the first dip of the film through a mercury surface raised its potential 5.72 volts, while the second raised it only an additional 0.47 volt. One dip of 144 Y layers on chromium gave a resulting positive film potential of more than 11 volts (which is the limit of our apparatus). A thin film of stearic acid was allowed to solidify on chromium and this was then dipped twice through a mercury surface. The first dip increased the potential of one spot by 2.40 volts, while the second dip increased it an additional 2.27 volts. Another spot increased by 5.57 volts and 3.77 volts, respectively. The surface of the clean chromium changed in potential very little with dipping, the values for the two dips being -0.05 volt and -0.01 volt.

From Eq. (5) one would expect that thicker films of paraffin on chromium dipped once into mercury would show higher film potentials.

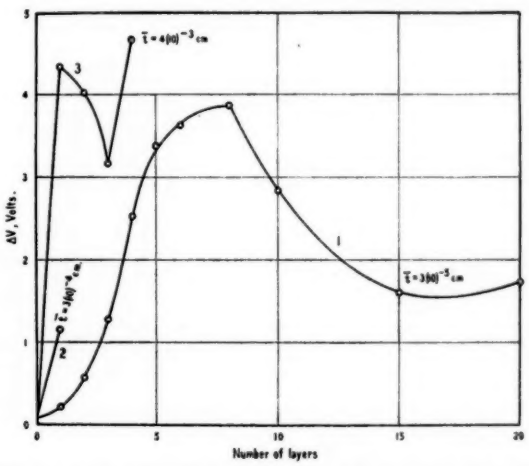

FIG. 7. Film potentials of X multilayers (solution 6) on three different thicknesses ($\bar{t}$) of paraffin (on gold).

[9] R. W. Goranson and W. A. Zisman, Phys. Rev. **53**, 668 (1938).

This was found to be the case. The film potential of a thin layer of paraffin on chromium dipped once into mercury increased by 0.14 volt; that of a thicker layer increased by 3.00 volts; while finally the potential of a very thick layer of paraffin increased by more than 11 volts, with the first dip in mercury.

In connection with these dipping experiments, it should be mentioned that it is exceedingly difficult to obtain a clean surface of mercury. Film potentials were induced on dielectrics on metals by dipping even when the mercury itself was grounded. It was found that all induced potentials on dielectrics decrease toward zero with time.

14. Effect of Stripping Layers from an X Multilayer

The effect on the potential obtained by dipping an X multilayer on paraffin on gold in and out through a clean surface of redistilled water is exhibited in Table II.

It is apparent that (1) a considerable fraction of the potential is removed by the first dip, and relatively little later, and (2) the first dip removes most of the large difference between the potential of the top and bottom of the film. This removal of the difference gives a hint, but does not prove, that a considerable percentage of the potential may be due to an outer surface charge. However, a part of the charge seems to lie deeper in the multilayer.

Stripping layers from the outside of a film may lower its potential very rapidly. Thus dipping an X multilayer once down and up through a clean surface of redistilled water lowered its potential of 2.36 volts by 651 mv, although talcum powder on the water indicated that only about two-tenths of a layer was removed on the down, and as much again on the up trip. The second and third dip lowered the potential much less, that is by 206 and 195 mv each. Fig. 8 shows that the loss of potential decreases with each dip. This type of behavior suggests that the charge leaks into the water. The effects produced by dipping into an alkaline subsolution have been described by Porter and Wyman.

Table II. *Effect of dipping an X multilayer on paraffin on gold through a clean surface of redistilled water. Potentials in millivolts.*

No. of Dips	0	1	2	3	4
Top	982	514	425	449	413
Bottom	1826	592	452	548	475

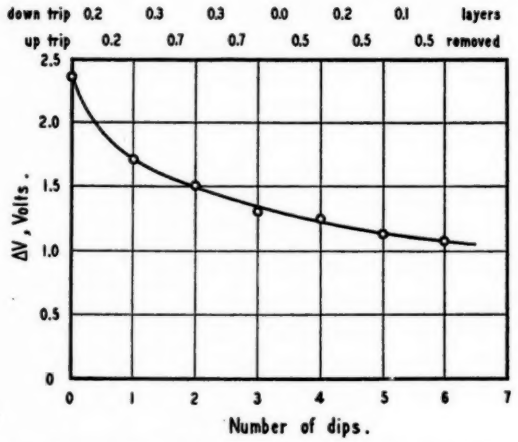

Fig. 8. Lowering of the film potential of an X multilayer on gold as it is successively dipped into the clean surface of redistilled water. The numerals at the top denote the fraction of the area of one normal X layer which was removed on each trip, as estimated by the recession of talcum powder on the water.

15. Effect of Time and Temperature on the Potential of X Multilayers

The effect of time on the potential of X multilayers at room temperature has been measured for about 50 different films. All of these exhibit the general relation shown in Fig. 9. This particular film at a mean room temperature of 23° decreased in potential by 50 percent in 14 days, and in 138 days decreased from the initial four volts to only 204 mv, or to five percent of the original potential. Porter and Wyman obtained about the same rate of decrease during a total period of ten days that is to 65 percent of the initial value.

When kept in an electric oven at 50°C the potential decreased approximately 50 times (Fig. 10), and at 85°C about 2500 times more rapidly than at room temperature and in very dry air at 50° the rate of decrease was almost the same. In an electric refrigerator at about −7°C the potential was lost more slowly than at room temperature.

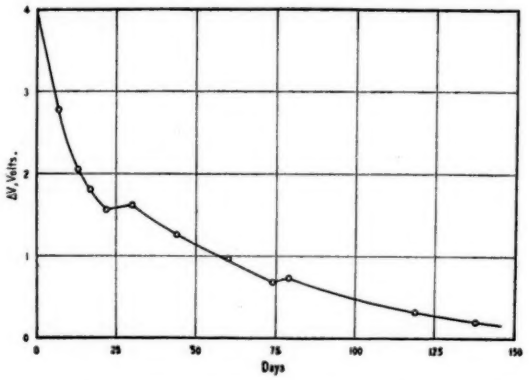

FIG. 9. The nearly exponential decay in potential of an X film of 100 layers (solution 1) stored in a tight wooden box at room temperature.

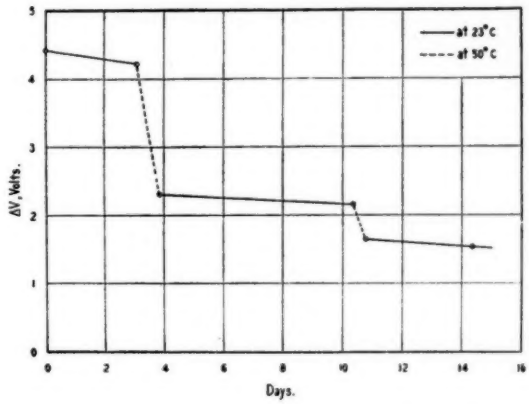

FIG. 10. The rapid decrease in film potential of an X multilayer made from solution 1, when heated in an electric oven at 50°C.

16. EFFECT OF ALPHA- AND GAMMA-RAYS

Bikerman and Schulman[10] have investigated the effects of α- and x-rays on the potentials of X films, but since they give no data as to the magnitude of the effects, one of our sets of values is given below.

A weak polonium source of alpha-rays placed one cm above an X multilayer decreased its potential to only five percent of its initial value in 15 minutes. This same general result was obtained with about ten other X films. A further 41-hour exposure to the same source of alpha-rays reduced the film potential of this X multilayer only seven mv. Alpha-rays quickly reduce to zero the film potential of paraffin on chromium dipped in mercury.

X films with 10, 20, 30 and 40 layers were irradiated for thirty minutes by gamma-rays from 0.94 mg of radium in solution coming through one cm of Pb, and then they were irradiated for 15 minutes by a weak polonium source of alpha-particles. It is apparent from Fig. 11 that the magnitude of the decrease of film potential during the first 15 minutes of irradiation by the gamma-rays is an almost constant fraction of the initial potential. Thus for 40, 30, 20 and 10 layers the potential decrease is respectively 29, 21, 24 and 26 percent. For the second 15 minutes, however, the potential decrement is respectively 90, 78, 97 and 71 mv, and while the values are somewhat irregular, they exhibit no apparent dependence on the original potential. The subsequent irradiation by alpha-rays also lowered the potential by an amount independent of the value of the initial potential, and this was reduced much more slowly than when a similar new film was initially irradiated with alpha-rays.

This behavior suggests that the X multilayers have a surface charge on the outer layer, and that this is removed rapidly, with the rate of leakage of the charge proportional to the potential, while the charges removed later are

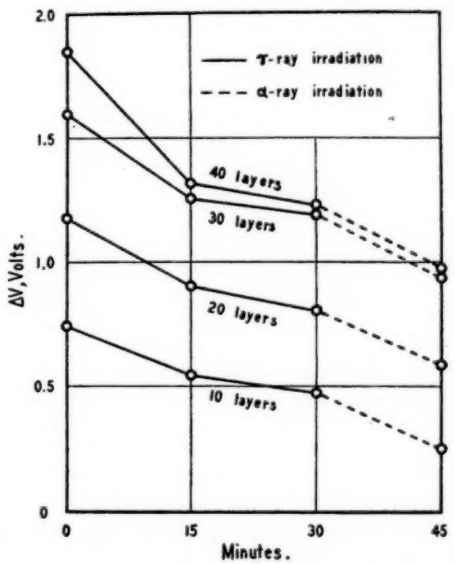

FIG. 11. The rapid decrease in film potential of X multilayers on gold made from solution 6, when exposed to gamma- and alpha-rays.

[10] J. J. Bikerman and J. H. Schulman, Phys. Rev. **53**, 909 (1938).

more deeply imbedded and their rate of removal is much less influenced by the potential.

17. Effect of Emanation from a Thorium Salt

X films of 10, 20, 30 and 40, layers on gold made from solution 2 were exposed to the emanation from about five grams of $Th(NO_3)_4 \cdot 12H_2O$ at one cm distance in air for 15 minutes. The top section of Fig. 12 shows the resulting large decrease in film potential of the X layers toward the thorium salt, and the bottom section of the figure shows the much smaller decrease of the potential of the X layers on the other side of the gold (0.025 cm thick). This difference indicates the absorption of alpha-particles by the gold.

18. Contact Potentials of Gold During Electrolysis

The changes in contact potential of two clean gold plates during electrolysis in $3(10)^{-3}$ m $AlCl_3 \cdot 6H_2O$, are exhibited in Fig. 13. The second measurement was made after the two gold plates had been immersed in the solution for one minute with no electric field between them. A more positive potential by about 65 mv

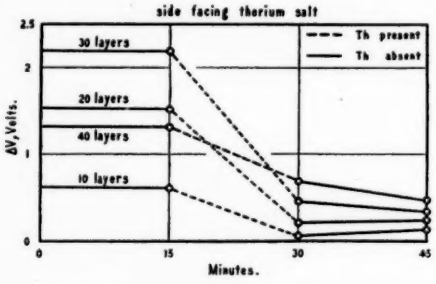

Fig. 12. The top section shows the large decrease in film potential of X layers on gold (solution 2) when placed in air one cm from a thin layer about five grams of $Th(NO_3)_4 \cdot 12H_2O$ for 15 minutes. The bottom section shows the much smaller decrease in potential of the X layers on the other side of the gold (0.025 cm thick).

was found in several other similar experiments with this same solution.

During succeeding immersions the gold plates were held parallel and nearly one cm apart and the known potential of a dry cell was applied between them. As was expected, the contact potential of the cathode measured in air after removal from the solution became more positive, while that of the anode became more negative. As is apparent from the figure, the first minute

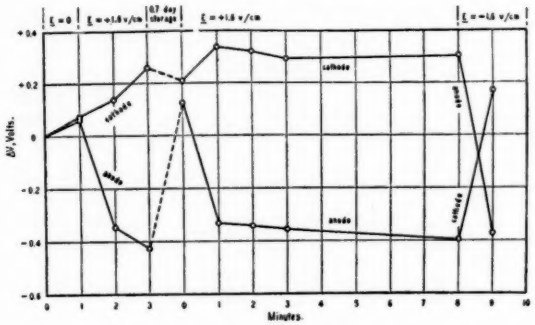

Fig. 13. Change in contact potential of two clean gold plates after use as electrodes during the electrolysis of $3(10)^{-3}$ m $AlCl_3 \cdot 6H_2O$.

of electrolysis produced almost all of the change in potential.

The contact potentials of the two gold plates were reversed in sign after one minute of electrolysis with the battery connections reversed, as is shown in the figure. A repetition of the above experiment, after the gold plates were covered with a thin layer of paraffin, gave much higher potentials, since the adsorbed ions were farther from the gold plates (Eq. (5)).

19. Immersion of Gold, Paraffin on Gold, and X Films on Gold in Various Solutions

Some experiments were carried out on the immersion of the surfaces of three different materials in four different solutions to see how much the adsorbed ions affected the film potentials. The three original surfaces were clean gold, paraffin on gold, and an X film on gold. The four solutions were:

(1) $3(10)^{-3}$ m $N(C_2H_5)_4Cl$ (pH = 4.75);
(2) $3(10)^{-3}$ m KCNS (pH = 6.37);
(3) $3(10)^{-3}$ m $AlCl_3 \cdot 6H_2O$ (pH = 3.86);
(4) $3(10)^{-4}$ m $NaC_{16}H_{33}SO_4$ (pH = 6.10).

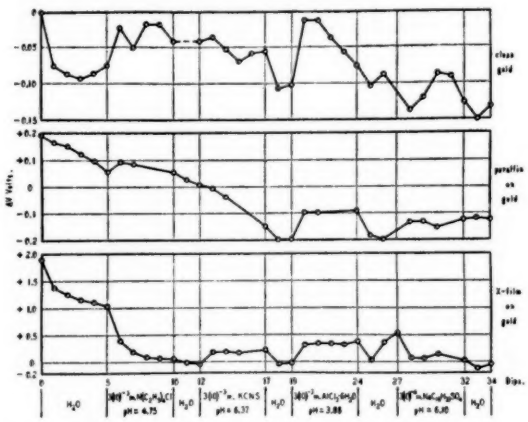

FIG. 14. Changes in potential of three different surfaces during one-minute immersions in four different solutions and in redistilled water.

The surface of each solution was swept clean with a barrier just before each immersion. Immersions of one minute duration were repeated until the general trend of the potential change could be determined. Fig. 14 is a summary of the effects. The curves vary widely with changes in the condition of the surface, so the figure is given only to illustrate what may occur.

20. POTENTIAL AND CAPACITY RELATIONS

In the case of the multilayers which exhibit a potential increment of 100 mv per layer the density of surface charge is 287 e.s.u. or $6\times10^{11}e$ charges per sq. cm or one positive charge for 830 stearate groups. The capacity is 0.9 microfarads per cm^2 if one X film is deposited on the metal, or $0.9/N$ for a larger number of layers. The value of the field is 4×10^5 volts per cm. We have found that in some instances the rapid drop in the potential of certain X monolayers as more layers are added is associated with a lowered value of pH, but in some other cases the effect is unexplained. It should be pointed out that while a field of four hundred thousand volts per cm is not sufficient to pull electrons out of a metal, it may be possible that it is sufficient to pull them out of a metal into a dielectric.

MARCH, 1939 JOURNAL OF CHEMICAL PHYSICS VOLUME 7

Experimental Evidence for Incomplete Rotational Excitation in Diatomic Gases at Ordinary Temperatures and Pressures[1]

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(Received January 18, 1939)

IN SOME recent studies of flame propagation we ignited mixtures of carbon monoxide and oxygen at the center of a spherical vessel and made simultaneous continuous records of the diameter of the spherical flame and the pressure in the vessel from the moment of ignition until the flame had grown to about one-half the vessel diameter. The observed pressures were always higher than the pressures calculated from thermochemical data. This indicates that the translational energy content of the gas exceeds that corresponding to thermodynamic equilibrium at the expense of internal energy (rotation and vibration). In attempting to ascribe this condition to the burned gas alone a deficiency of internal energy corresponding to almost complete absence of molecular vibration had to be assumed; this is inconsistent with the knowledge that the molecules emerge from the elementary reactions with highly excited internal degrees of freedom, and also with the close agreement found between calculated and experimental maximum pressures in spherical vessels.[2] This made it appear probable that there was a deficiency of internal energy in the adiabatically

[1] Published by permission of the Director, Bureau of Mines, United States Department of the Interior, and the Director, Coal Research Laboratory, Carnegie Institute of Technology. (Not subject to copyright.)

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[2] B. Lewis and G. von Elbe, J. Chem. Phys. 3, 63 (1935).

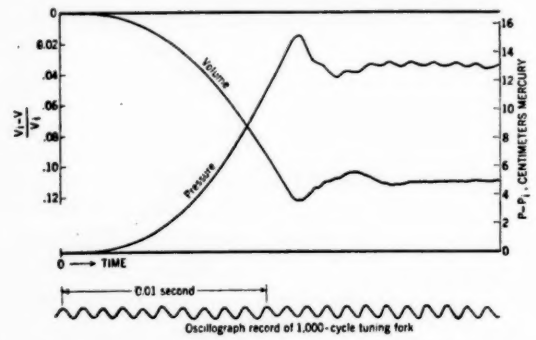

FIG. 1. Photographic record of volume and pressure changes during compression of oxygen gas. V_i and P_i = initial volume and pressure. V and P = volume and pressure at any time. $P_i = 74.40$ cm Hg. Initial temperature = 23.3°C.

compressed unburned gas surrounding the spherical flame. Since the temperature of this gas increases only a few degrees above room temperature its internal energy consists almost entirely of rotation. Making reasonable assumptions concerning a possible deficiency of internal energy in the burned gas, the observed pressures demanded that the ratio, γ, of the specific heats at constant pressure and volume of the unburned gas be increased several units in the second decimal place above the equilibrium value of 1.40 for translation and rotation.

This incomplete rotational excitation was verified by the following experiment: The gas at room temperature and about one atmosphere pressure was enclosed in a sylphon bellows about one inch long and about two inches in diameter. To minimize heat loss the surface-to-volume ratio was decreased by filling the inside corrugations with live rubber. One end of the bellows was closed by a pressure indicator of the diaphragm type[3] and the other end by a plate that had a central shaft extending from its outer face. A section of this shaft consisted of soft iron, which formed the plunger of a solenoid. On energizing the solenoid the shaft moved and compressed the bellows until arrested by a cushioned stop. At the other end of the shaft was mounted a conical steel bushing which on moving forward actuated a mirror for photographically recording the movement of the shaft, that is, the change in volume, on a rotating film. The pressure change was recorded simultaneously on the same film.

A typical record is shown in Fig. 1. It is noted that both curves reach the peaks at the same time, showing that the pressure indicator responded instantaneously. The latter was calibrated against a mercury manometer and the volume indicator by slow isothermal compression, using the gas law. Test runs with argon yielded a value of $\gamma = 1.65$. That the difference between this value and the theoretical value 1.67 is due to heat loss was confirmed by a comparison of the results of experiments with helium as well as the cooling curves following the pressure peaks for both gases. The rebound from the cushioned stop accounts for the irregularities in the volume curve immediately following the peak. These irregularities are reflected in the pressure curve, indicating that they correspond to actual volume changes. Superimposed on this part of the pressure curve are oscillations arising from vibrations of the gas or the diaphragm. The cooling rate is obtained from the slope by averaging over the oscillations.

For oxygen, nitrogen and carbon monoxide the values of γ were found to exceed 1.40 by several units in the second decimal, even without correcting for the small heat loss. The heat-loss correction was estimated to be about 0.01. For oxygen the corrected values were found to be 1.43 for a time of 12 milliseconds between the beginning and end of the compression and 1.46 for 7.5 milliseconds, corresponding to an energy deficiency of rotational excitation of 20 percent and 33 percent, respectively. These values of γ are averages taken over the steep part of the curves during the last half of the period of compression. They show that with decreasing compression rates γ tends toward the equilibrium value, as expected.

For N_2 and CO γ was found to be almost identical with the value for O_2. For N_2 it was a little higher by approximately 0.005 for the above compression times.

The contribution of the vibrational excitation at room temperature affects only the third decimal place of γ and is, therefore, not noticeable in these experiments.

A more detailed description of this work will be published later.

[3] An adaptation of a former design (B. Lewis and G. von Elbe, J. Am. Chem. Soc. **55**, 504 (1933)) to measure small pressure changes.

Corrections to Paper "The Role of Free Radicals in Elementary Organic Reactions"[1]

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(Received February 4, 1939)

IN OUR paper on free radicals, we have formulated and applied what we call the Principle of Least Motion in Chemical Reactions. We pointed out, of course, that this principle is by no means entirely new. Since the publication of our paper, it has come to our notice, however, that a formulation very closely resembling the one given by ourselves has been proposed by Peytral.[2] Though we agree with her formulation of the principle, we believe that the reactions that we selected for discussion are better illustrations of the principle than those given by Peytral.

One of the main applications of the principle has been the statement that a shielded carbon atom, that is, one bound to four other atoms, can be attacked only if an activation energy of not less than about 40 calories is available. We now believe that our generalization has not been completely justified, since the estimation of 40 calories was based on considerations concerning methane. Caution is needed, particularly if the bond between the carbon atom and any of its neighbors is rather weak. Thus if a C−I bond is present, 40 calories are sufficient to sever this bond; the three other substituents and the carbon atom will then, according to our own statements, have their equilibrium positions in one plane, and the carbon atom will be as exposed as a carbon atom with a double bond. The actual energy necessary to expose the atom will be, therefore, the 40 calories mentioned above, minus the energy that can be gained by bringing the severed iodine atom back towards the radical while keeping the carbon atom and its three neighbors in a plane. The actual mistake that entered into the reasoning in our paper was that we considered the motion of only those substituents which were being pushed into the plane with the carbon atom, and we disregarded the motion of the fourth substituent. This procedure is, we believe, permissible if the fourth particle is bound strongly to the carbon, e.g., a C−H bond, but it is not allowable if the fourth substituent is bound by rather weak forces.

In view of the above discussion, we believe that the recemization of optically active compounds containing a C−I bond might proceed according to the mechanism proposed by Ogg and Polanyi.[3]

[1] F. O. Rice and E. Teller, J. Chem. Phys. **6**, 489 (1938).
[2] Peytral, Comptes rendus. **197**, 831 (1924); Bull. soc. chim. **29**, 44 (1921).
[3] R. A. Ogg and M. Polanyi, Trans. Faraday Soc. **31**, 482 (1935).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Statistical Theory of Condensation Phenomena

Mayer and his co-workers[1] and subsequently Kahn and Uhlenbeck[2] and Born and Fuchs[3] have developed an interesting theory of condensation phenomena, which, however, because of its mathematical intricacy will hardly appeal to the experimental physicist or chemist.

I wish to show in this note that essentially the same results can be obtained in a quite elementary way with the help of the statistical theory of chemical equilibrium in a gas mixture.

The simplification underlying the application of this theory to the problem of the condensation of a vapor, consists in neglecting intermediary degrees of binding between its atoms (we limit ourselves to the case of a monoatomic substance). These atoms will be considered accordingly either as entirely free, or as bound together into diatomic "molecules," or into triatomic "molecules" and so on. The number of "molecules" consisting of g atoms will be denoted with N_g. For sufficiently large values of g these "molecules" will actually behave as small drops of the liquid or small crystals of the solid phase. For the sake of simplicity, the existence of different "isomeric" forms of the same g-atomic molecule (differing with respect to shape and size) will be neglected.* If moreover we neglect the mutual action between different molecules and treat the whole system as an ideal gas mixture, the ratios between the numbers N_g can be determined by the ordinary mass action law

$$N_g/N_1^g = F_g/F_1^g, \tag{1}$$

where F_g is the partition function for one molecule of the given species. We have

$$F_1 = V\left(\frac{2\pi m_1 kT}{h^2}\right)^{\frac{3}{2}} e^{-U/kT}, \tag{2}$$

where V is the total volume occupied by the system, m_1 is the mass of an atom, and U its potential energy in the free state ($=0$).

We have further $F_g = e^{-\psi_g/kT}$ where ψ_g is the free energy of the molecules of the species g referred to one of them. For very large values of g($g\sim 10^3$, say) ψ_g must be proportional to g, so that we can put in this case $\psi_g = U' \cdot g$ and consequently

$$N_g = \xi^g \qquad (g \gg 1), \tag{3}$$

where

$$\xi = \frac{N_1}{V}\left(\frac{2\pi m_1 kT}{h^2}\right)^{-\frac{3}{2}} e^{(U-U')/kT}. \tag{3a}$$

So long as $\xi<1$ we have to do with an unsaturated vapor of the substance under consideration (contrary to the current opinion, such a vapor in the case of a monoatomic substance consists partially of larger atomic groupings). The case $\xi>1$ corresponds to an over-saturated vapor. The saturation or condensation point is thus determined by the condition $\xi=1$. Putting $U' = U_0' - 3kT \lg h\nu/kT$, where U_0' is the energy per atom at $T=0$ and ν is an average vibration frequency (this formula can be applied both to liquid drops and to crystals), we can rewrite this condition in the form

$$\frac{N_1}{V} = \left(\frac{2\pi m_1 \nu_1^2}{kT}\right)^{\frac{3}{2}} e^{-(U-U_0')/kT}, \tag{4}$$

which agrees with the usual formula for the concentration of the saturated vapor of a monoatomic substance as a function of the temperature (with the minor difference that N_1/V is not the *total* concentration, but the *partial* concentration of the monoatomic portion of the vapor).

If g is not too large, the surface free energy of the droplets, or crystals, must be taken into account by adding to ψ_g a term proportional to $g^{\frac{2}{3}}$. Denoting the proportionality coefficient with α we obtain instead of Eq. (3)

$$N_g = \xi^g e^{-\alpha g^{\frac{2}{3}}/kT}. \tag{5}$$

If $\xi<1$ this expression decreases monotonically with increase of g. In the contrary, case ($\xi>1$) it displays a minimum for a value of g given by

$$\lg \xi = \frac{2}{3}\frac{\alpha}{kTg^{\frac{1}{3}}}. \tag{6}$$

Since at a given temperature ξ, according to Eq. (3), is proportional to the concentration N_1/V and consequently to the pressure p of the vapor (or more exactly to the partial pressure of its monoatomic component) and since $\xi=1$ corresponds to the saturation pressure $p=p_0$, the preceding formula can be written in the form

$$\lg \frac{p}{p_0} = \frac{2}{3}\frac{\alpha}{kTg^{\frac{1}{3}}}. \tag{6a}$$

In the case of a spherical droplet it reduces to the well-known Thomson formula for the vapor pressure over the surface of a droplet as a function of its radius (which is proportional to $g^{\frac{1}{3}}$).

Substituting the expression (6) into (5) we obtain for the minimum value of N_g

$$N_g = e^{-\frac{1}{2}\alpha g^{\frac{2}{3}}/kT}, \tag{7}$$

which is just Volmer's formula for the velocity of condensation of an oversaturated vapor resulting from the formation and further growth of droplets of the critical size determined by (6a). We thus see that our simple theory not only gives an accurate description of the condensation phenomenon, but also accounts for the phenomena connected with oversaturation.

The theory could be improved by taking into account the mutual action between the "molecules" of our "gas-mixture." This can be done in a formal way by multiplying the various N_g's with the corresponding "activity coefficients." Practically this correction must result in a tendency of the larger "molecules" to coalesce into a single mass—liquid or crystalline, as the case may be.

The preceding theory can be applied with a few modifications to the phenomena of *polymerization* (i.e., the formation of large chain-like macromolecules), which can be considered as a kind of condensation (in the physical sense of the term) in one dimension, the van der Waals forces being replaced by valence forces. The residual van der Waals attraction between different macromolecules will be relatively ineffective in their coalescence to larger units. This case is also distinguished by the absence of oversaturation (or overcooling) phenomena, the free energy of the two ends of a macromolecule being independent of its size.

A full account of the theory will be published elsewhere.

J. FRENKEL

Physico-Technical Institute,
Leningrad, U. S. S. R.,
November, 1938.

* They can easily be accounted for approximately if one limits himself to structures which are not very different from the normal ones, i.e., those corresponding to the minimum value of the energy for any given value of g. The complications of Mayer's theory are connected mainly with intermediate structures, corresponding to large deviations from the normal.

[1] J. E. Mayer, J. Chem. Phys. **5**, 67 (1937). J. E. Mayer and S. F. Harrison, J. Chem. Phys. **6**, 87, 101 (1938).
[2] G. E. Uhlenbeck and B. Kahn, Physica **5**, 399 (1938).
[3] M. Born and R. Fuchs, Proc. Roy Soc. **166**, 391 (1938).

Inhibition of Crystallization of Rubber by High Pressure

Bekkedahl[1] has shown that crude rubber at atmospheric pressure freezes in the temperature range from −40° to +10°C and melts in the temperature range from 6° to 16°C. The transition is from amorphous I to crystalline I which is the stable modification between −72° and 6°C. His measurements of the freezing at 0°C showed that about 280 hours were necessary for completion of the transition, the volume decreasing by 2.2 percent in such a manner that the volume-time curve was S-shaped.

This communication reports the inhibition of crystallization at high pressure. Crude smoked sheets were packed tightly in a pressure chamber and isopropyl alcohol was used to transmit the pressure. The chamber was kept at 0°C in a well-circulated ice bath. A pressure of 8000 kg/cm² was applied and its constancy observed over a period of 14 days. The sensitivity of the manganin gauge used for pressure measurement was such that changes of 5 kg/cm² were detectable. Outside of slight erratic pressure changes caused by change of temperature around part of the press that was not kept at 0°, "no change of pressure due to crystallization was detected during the 14 days." Examination of the rubber immediately after pressure was released showed that it was still in the amorphous state.

Since the specific volume of amorphous I is greater than that of crystalline I, pressure raises the transition point and it can be said that the inhibition is due to supercooling. Using the data of Bekkedahl,[1] and Bekkedahl and Matheson[2] for melting temperature, change of specific volume on melting, and heat of fusion, computation by Clapeyron's equation shows that the melting point of crystalline I is of the order of 400°C at 8000 kg/cm². The inhibition of crystallization appears to be an effect of high viscosity of amorphous I at high pressure. Extremely high viscosities have been observed[3] in complicated organic compounds under pressure and when it is considered that the molecular aggregates in crude rubber may number several hundred chemical molecules, it is to be expected that the viscosity of amorphous rubber at 8000 kg/cm² may be increased enormously. Staudinger has computed an average molecular weight of a raw rubber in the hundred thousands, a value indicating that the pressure coefficient of viscosity must be very high since it is known that this coefficient increases with molecular weight.

The transition from crystalline I to amorphous I at high pressure appears to be an equilibrium phenomenon, however. Samples of smoked sheet crystallized at atmospheric pressure were observed to melt at 77.5°C at a pressure of 1270 kg/cm². dT_m/dp is then 0.0484 as compared with a calculated value of 0.0518°C/kg/cm² by Clapeyron's equation at atmospheric pressure on the assumption that the normal transition point is 16°C. Melting took place slowly, approximately five minutes being required for completion. If the normal melting point of the rubber is taken at 11° rather than 16°C, the above value for melting under pressure will be increased accordingly.

Because of high viscosity it would appear that amorphous I can be kept in the metastable state over a long period of time at 8000 kg/cm². Bekkedahl concluded that the rate of crystallization of rubber below −50°C at atmospheric pressure was too small to be measured during several weeks of observation. Examples of delayed equilibrium are well known. Deville observed a transition in sulphur over a period of 2 years, and it has been observed that the transition from white to gray tin at 18°C may require several centuries for completion under ordinary conditions. Many polymorphic changes at high pressures have been found by Tammann, Bridgman, and Cohen to take place very slowly, although the transitions are quite different in nature from the one discussed here.

The writer is indebted to Dr. Lawrence Wood of the National Bureau of Standards for suggesting these experiments and contributing much helpful adivce.

R. B. Dow

The Pennsylvania State College,
State College, Pennsylvania,
February 1, 1939.

[1] Norman Bekkedahl, Nat. Bur. Stand. J. Research **13**, 411 (1934).
[2] Norman Bekkedahl and Harry Matheson, Nat. Bur. Stand. J. Research **15**, 512 (1935).
[3] R. B. Dow, H. E. Morgan and M. R. Fenske, Ind. Eng. Chem. **29**, 1078 (1937).

On Transport Phenomena in the Cage Model of Liquids*

The liquid cage model developed from geometrical considerations, based on x-ray investigations, as well as from kinetical and statistical ideas, was used by Rabinowitch[1] in order to describe the diffusion process in quasi-crystalline liquids. Using the theory of holes he obtains an expression for the diffusion constant D as function of the vibration frequency ν of a molecule; of the distance **a** between adjacent lattice points; of the crystallographical coordination number n, where $6 \leqq n \leqq 12$; and finally of the hole energy U, which is the energy necessary for the enclosed molecule in order to escape through the cage. U is therefore a fraction of the internal evaporation energy.

Recently Polissar[2] investigated the electrical conductivity of dilute ionic solutions on the basis of the abovementioned model.

In the following we shall derive along similar lines a formula for the internal friction η of a simple quasi-crystalline liquid.

A single molecule undergoes m_0 displacements per unit time of length **a** so that

$$m_0 = 6D/a^2. \tag{1}$$

Now if a shearing force **f** per unit area is applied, the number of jumps in the direction of the "field" is increased to m_+, in the opposite direction decreased to m_-. The difference multiplied by the length **a** of a jump gives the relative velocity Δv between two layers, caused by the applied stress. Therefore one obtains for a Newtonian liquid

$$\eta = \frac{l\sigma}{\Delta v} = \frac{l\sigma}{a(m_+ - m_-)}, \tag{2}$$

where σ represents the distance between the two layers. In order to compute the denominator, we notice that the energy change of the molecule amounts to $\pm lga/2$, where q is the area occupied by a single particle, and $a/2$ half of the breadth of the potential barrier formed by the cage. By reasons of the isotropy of the fluid, in the undisturbed state $\frac{1}{6}$ in the average of all the displacements occur in either of the directions $\pm l$, $\frac{2}{3}$ in the other two orthogonal directions. Then from statistical mechanics

$$m_+ - m_- = \frac{m_0}{6}(e^{lga/2kT} - e^{-lga/2kT}) = \frac{m_0}{6}\frac{lga}{kT}$$

after expansion up to the first power of the exponent, and using (1)

$$\eta = kT\sigma/gD. \tag{3}$$

This relation between the viscosity and the diffusion coefficient replaces the corresponding hydrodynamical equation in the case where all the particles are of comparable size. It was already derived by Eyring[3] in applying the transition state method. This is to be expected, as in both treatments the idea of a kind of activation process is fundamental. Considering that $g\sigma = V/N$ (N, Avogadro's number, V, molar volume) and putting $\sigma = a$ one gets from (3)

$$\eta = (RT/V)(a^2/D). \tag{3a}$$

The improved Rabinowitch expression for the diffusion constant reads as follows:

$$D = \frac{na^2}{6}\nu e^{-U/RT}.$$

In the derivation both particles and holes were considered as oscillators of equal frequencies and only classical partition functions used. Substituting for D in the formula (3a) it finally follows for the viscosity:

$$\eta = \frac{6}{n}\frac{RT}{V\nu}e^{U/RT}. \tag{3b}$$

If one takes into account the second of the assumptions mentioned above, (3b) also is substantially identical with Eyring's corresponding expression. It differs only by the factor $6/n$ which enters as consequence of the cage concept. Assuming different phase volumes for holes and particles,[4] (3b) has to be multiplied by a factor $(1+\gamma T)^3$, where γ is a measure for the unharmonicity of the particle vibrations and can be estimated from deviations from the Dulong-Petit rule at high temperatures.

It would not be difficult to extend these considerations to the calculation of the heat conductivity λ. But whereas one gets rather reasonable results for η, the computed λ-values are by far too small. These discrepancies show that the cage model in its present form is too simple to give an adequate description of the complicated process of energy transport in liquids.

It is a pleasure for the author to acknowledge a grant from the Faculty Fellowship Fund to carry on this work in Professor V. K. LaMer's Laboratory.

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January 23, 1939.

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

[1] Rabinowitch, Trans. Faraday Soc. **33**, 1225 (1937). Compare also Mark and Simha, Naturwiss. **25**, 833 (1937).
[2] Polissar, J. Chem. Phys. **6**, 833 (1938).
[3] Eyring, J. Chem. Phys. **4**, 283 (1936).
[4] Mark and Simha, reference 1.

Concerning the Existence of a Two-Phase Region in the Ordering Process

Superlattice formation is usually pictured as a process which takes place homogeneously within a single phase.[1] Above the critical temperature, the degree of order is zero, below that it rapidly but continuously becomes more perfect. However, it is plausible thermodynamically that there should be a two-phase region separating the ordered and disordered states at all compositions except the most stable one. A number of investigators have reported x-ray photographs showing the simultaneous presence of ordered and disordered phases in samples annealed near the critical temperature. However, it has not been demonstrated whether these represent equilibrium or merely incomplete reactions. Electrical resistance measurements show the existence of hysteresis in the ordering process, indicating that equilibrium is difficult to obtain.

Besides the intrinsic importance of the subject, a decision must be made in representing superlattices on equilibrium

diagrams. We have tested for the attainment of equilibrium by approaching it from both sides. In the iron-palladium system[2] there is apparently a rather wide two-phase region in the FePd superlattice in a sample containing 51.9 atomic percent palladium. (This is a face-centered tetragonal superlattice with the structure of AuCu. Its maximum stability occurs near 60 atomic percent palladium.) This sample contained a disordered face-centered-cubic phase along with an ordered face-centered-tetragonal phase when annealed for a number of days at 675°C, and also at 700°C.

A portion of the sample was annealed for a week at 600°C and quenched. An x-ray diffraction photograph showed it to be completely ordered. Two other portions were annealed for two days at 750°C. One of them was quenched and found to be completely disordered. The other was left in the furnace, which was cooled to 690°C. At this point, the completely ordered sample was inserted and both were annealed for 15 days before quenching. The ordered sample had become partly disordered, two phases being present. However, the disordered sample remained unchanged. This renders it probable that disorder is the equilibrium condition at this temperature and that the two-phase picture represented an incomplete reaction. Hence, none of the two-phase pictures reported in the literature can be regarded as evidence for the existence of an equilibrium two-phase region, although the absence of such a region would be difficult to prove.

It is interesting that while equilibrium can readily be attained above and below the critical temperature, it is difficult to attain near it.

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Harvard University,
Cambridge, Massachusetts,
January 17, 1939.

[1] W. L. Bragg and E. J. Williams, Proc. Roy. Soc. **A145**, 699 (1934).
[2] R. Hultgren and C. A. Zapffe, Zeits. f. Krist. **A99**, 509 (1938).
Metals Technology (to be published).

Viscosity of Two-Dimensional Systems: Effect of Pressure and Temperature, and Detection of Phase Transitions in Monolayers

The viscosity of monolayers on an aqueous subsolution is highly dependent upon the closeness and the type of packing of the molecules in the film. Both of these are affected by *p*H and the presence of ions which interact with the molecules in the monolayer, and in addition are functions of the pressure and the temperature. Investigations of the surface viscosity of the long chain normal saturated fatty acids have revealed the following relations (Fig. 1):

(1) From the lowest pressures investigated up to some definite pressure, which is of the order of 18 dynes per cm at 25, the *logarithm* of the film viscosity (σ) is proportional to the pressure (f) or

$$\log \sigma = \log \sigma_0 + kf.$$

(2) The viscosity of the liquid monolayers rises rapidly with the length of the hydrocarbon chain.

(3) The liquid or low pressure condensed films exhibit a Newtonian viscosity. These are condensed films of higher compressibility.

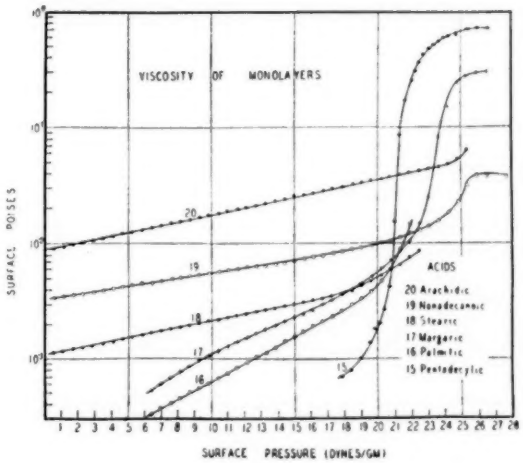

FIG. 1.

(4) If the film pressure on a liquid condensed film is increased at constant temperature it may undergo a phase transition into a condensed film of low compressibility, which has usually been designated as solid. We find that the films of the acids exhibit a non-Newtonian viscosity, as in the case of the similar alcohols.[1] That is the viscosity varies with the rate of shear, so such films may be designated by the term "plastic" if it is remembered that it has not been shown that such films give a yield point.

(5) Contrary to what is found for liquid-condensed films, those in the "solid-plastic" state decrease rapidly in viscosity as the length of the chain increases, as was found with the alcohols.

(6) From (2) and (5) it follows that the increase in viscosity with pressure in the neighborhood of the phase transition, Liquid Condensed→Plastic Solid Condensed, has a high magnitude for the short molecules, and a low magnitude for films which consist of long molecules. Thus with pentadecylic acid (15 C) the viscosity increases about a thousand times, but less than four times if the chain is increased to 19 C atoms.

(7) As the pressure is increased above that for the transition the viscosity increases less and less rapidly until it becomes approximately constant.

(8) The liquid-condensed films have a very much lower viscosity with the acids than with the corresponding alcohols, and the factor has the general order of 20 to 30. This is related to the fact that the molecules are packed much less tightly in the acid than in the alcohol monolayers. Thus the limiting value of the area at zero pressure at 25°C is 24.4 sq. A for the 18 C acid, but only 21.8 sq. A for the 18 C alcohol.

(9) However, in the "solid plastic" state the viscosities of the acid and of the alcohol films are of the same general order of magnitude for the same length of molecule, but in this state the molecular packing is also about the same.

(10) It may be noted in Fig. 1 that only the curves for the acids which contain in the molecule an odd number of carbon atoms are continued into the "solid-plastic" state. This indicates that the transition, Liquid Condensed→

"Solid Plastic," occurs much more readily if the number of carbon atoms is odd than if it is even. The viscosity measurements take a long time for their completion. If the films are compressed with sufficient rapidity the "even" films also undergo the transformation.

(11) A decrease of temperature from 25°C to 10°C multiplied the viscosity by 5, an extremely great change, but an increase of temperature above 25 lowered the viscosity much less rapidly. This experiment was carried out with arachidic acid (20 C atoms), and the curves remained practically parallel to that given for 25°C between 10° and 31.5°C.

(12) At 10°C the viscosity of the liquid condensed film of arachidic acid became non-Newtonian at pressures above 11 dynes per cm while the phase transition did not occur until it had increased to 25 dynes per cm. A similar effect has been observed in the earlier work with stearyl alcohol at 20°C.

If a gaseous film of pentadecylic acid is compressed at constant temperature it changes first to an expanded and then with a moderately sharp transition to an intermediate state. Endeavors have been made by others to determine if this changes to a liquid-condensed, and finally transforms into a "solid" film, but such attempts have been unsuccessful. However the viscosity relations exhibit the transition, Liquid→"Solid," at 25°C, 21.35 dynes per cm and this is at an area of 20.5 sq. A. Thus the viscosity relations reveal with great ease transitions which are not commonly found in the pressure-area relations.

Our experimental data on the effect of pressure agree remarkably well with the theory of Moore and Eyring,[2] since our Eq. (1) is analogous to their Eq. (3)

$$\log \sigma = \log \frac{h}{a} + \frac{\Delta F\ddagger}{k'T}$$

in which the value of $\Delta F\ddagger$ is given by their Eq. (6).

According to their general theory this energy ($\Delta F\ddagger$) involves two terms (1) the external work fa, and (2) the work of making a hole of area a against the internal pressure. Their $fa/k'T$ corresponds to our kf, in which $k = a/k'T$. The discussion of the theory will be given in a later communication.

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February 12, 1939.

[1] L. Fourt and W. D. Harkins, J. Phys. Chem. **42**, 897 (1938).
[2] W. J. Moore, Jr. and H. Eyring, J. Chem. Phys. **6**, 391 (1938).

A New Method for the Investigation of the Electrical Properties of Multilayers

A method, different from any applied earlier, seems to offer promise of revealing much that occurs in the production of a film potential when X or Y multilayers are built up on a metal at various values of pH of the subsolution utilized. This consists in measuring the electrical current, or charge, which passes between the metal slide upon which the film is deposited, during its up and down trips, and another (comparison) electrode of the same metal (gold), immersed in the solution. In using this method there are several difficulties which must be kept in mind.

(1) If one electrode has been in the solution for a long time (e.g. ½ hour), and the other is now dipped into the liquid, a relatively large current flows between them during the first few seconds, even after the slide has ceased its motion.

(2) If both electrodes have been (partly) immersed for a long time, a small current usually flows, probably because there are small differences in the metal surfaces or the adjacent solutions.

(3) A current passes between the electrodes while one of them is being dipped into the solution through a clean surface. During the down trip this flows in the opposite direction from that during the up trip. This current is due to the constant galvanic potential between the metal electrode and the solution, and the change in capacity during the dipping.

In the experiments current (2) is made zero by adjusting the depth of immersion of the comparison electrode. The disturbing current (1) disappears if both electrodes are immersed for a long period, or if several layers have been deposited on the slide, thus insulating it from the solution. The disturbing current (3) also decreases with the number of layers since the capacity between the electrode and the solution also decreases.

If it is desired to study the currents due to the first few layers, both electrodes should be dipped synchronously: one through the monolayer on the subsolution, and the other through a clean surface of the latter.

The first experiments consisted of dipping clean gold through the clean surface of a solution buffered at pH 9.4. Apart from currents (1), which become very small after the first few dips, there first appear, during both the up and down trips, currents of about the same magnitude but in opposite directions for the two. These currents show that the potential of the gold electrode is negative with respect to the solution. No currents flow if the slide emerges wet, as it may if the upward movement is very quick. This is because the electrical double layer of the gold and solution is removed with the wet slide, and is not disturbed as when the gold emerges dry.

During the deposition of X films at a pH of 9.4, there appear, apart from currents (1), quite the same currents as are produced by dipping clean gold through a clean surface of the solution, but the currents become smaller and change sign as the dippings increase. This reversal of sign takes place when the X film has attained a potential of about 0.4 volt. After this the currents have almost a constant value, or decrease slightly with the number of layers.

During the up trip the positive current flows from the comparison electrode through the solution to the X multilayer, and in the opposite direction on the down trip.

An X multilayer, with a positive charge on the outside layer may be dipped into the solution, when it is found that if the film potential before the dipping was greater than about 0.5 volt, say 2 volts, a positive current flows through the solution from the multilayer to the gold of the comparison electrode. If the system X multilayer-gold is now removed from the solution it exhibits a decrease of film

potential, the magnitude of which increases with the time of immersion. Thus the current during the down trip with X deposition, has the same direction as the discharging current specified here.

The total charge transferred during the down or up trip is of the same order of magnitude, as closely as could be calculated from the preliminary data, as the charge on the outer surface of the multilayer would need to be to give the measured film potential.

From the above it is not necessary to conclude that the film is completely charged during the down and discharged again on the up trip. It is possible that a double layer is formed between the surface of the film and the solution. In any event the potential with respect to the solution is reduced when the multilayer-metal system is in the solution.

If the slide is allowed to remain at rest at its deepest immersion, no current flows when the number of X layers is small, but with a larger number of layers a very small discharge current is observed. The increment of potential per layer of an X multilayer is known to decrease with the number of layers, so if the potential is due to a charge on the outermost layer only, this charge must also decrease at the same rate. It is possible that this is due to a partial discharge of the film during its building, through the action of the small currents just described.

In the production of Y films at pH 7.0 the relations are different. During the down trip the current always flows through the solution from the comparison electrode to the slide plus multilayer, and in the opposite direction during the up trip, until, usually, the film potential attains a value of about 0.2 volt. After this the potential does not increase, since now both currents fall to almost zero.

This communication is too short to present other relations, and these and all quantitative work will be presented in the complete paper.

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